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Extensão da Equação de Estado soft-SAFT para Sistemas Poliméricos

Extension of the soft-SAFT Equation of State for Polymer Systems

tese apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Doutor em Engenharia Química, realizada sob a orientação científica da Dr. Isabel Maria Delgado Jana Marrucho Ferreira, Professora Auxiliar do Departamento de Química da Universidade de Aveiro e do Dr. João Manuel da Costa Araújo Pereira Coutinho Professor Associado do Departamento de Química da Universidade de Aveiro

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palavras-chave

Polímeros, Modelação, modelos GE, Equação de Estado, SAFT, equilíbrio de fases

resumo

Ao longo da história da termodinâmica moderna, a procura de um modelo matemático que permita descrever o equilíbrio de fases de polímeros tem sido constante. Industrialmente, o desenvolvimento de um modelo de equilíbrio de fases de sistemas poliméricos reveste-se de uma enorme importância, especialmente no processo de fabrico propriamente dito onde o polímero é misturado com solvente (no caso da polimerização em solução) e com monómero. Podem ainda existir outros compostos em solução, tais como surfactantes e/ou iniciadores da reacção de polimerização, embora a sua concentração seja normalmente tão baixa que não afecta o equilíbrio de fases de um modo significativo. A previsão do comportamento do equilíbrio de fases é também importante no passo de purificação do polímero, onde este tem que ser separado do monómero que não reagiu e é recirculado para o reactor de polimerização. Esta tese constitui mais um passo no sentido de aprofundar o desenvolvimento de tais modelos.

O principal problema na modelação termodinâmica de polímeros é o facto de estes não poderem ser decompostos em termos matemáticos, físicos ou químicos tal como outros tipos de moléculas, já que os polímeros são diferentes não só na estrutura química como também nas eventuais ramificações, na massa molecular ou na distribuição de massas moleculares, entre outras propriedades. O objectivo deste trabalho é descrever o equilíbrio de fases de misturas envolvendo polímeros usando vários modelos que pertencem a diferentes tipos de abordagem, nomeadamente modelos de energia livre baseados no modelo “Universal Quasi Chemical Activity Coefficient” (UNIQUAC), e equações de estado, tais como a “Statistical Associating Fluid Theory” (SAFT), em particular as versões soft-SAFT e PC-SAFT.

Com o objectivo de obter um conhecimento mais aprofundado do equilíbrio de fases de polímeros, o estudo inicia-se quando possível na caracterização dos seus precursores, i. e., monómeros e oligómeros. Este facto permitiu a compreensão da evolução das propriedades termodinâmicas com a massa molecular numa dada série de compostos, tais como os *n*-alcanos e os etilenoglicois, ocasionando o desenvolvimento de esquemas de correlação e possibilitando o uso da SAFT de uma maneira preditiva.

Especial atenção foi dada a sistemas polímero-solvente com associação, o qual foi programado e testado pela primeira vez na soft-SAFT. Os modelos SAFT provaram que conseguem vários tipos de equilíbrio de fases, nomeadamente equilíbrio líquido-líquido com temperatura critica superior de solução e temperatura critica inferior de solução, liquido-vapor e equilíbrio gás-liquido.

keywords Polymers, Modeling, GE models, Equations of State, SAFT, Phase Equilibria

abstract

Throughout the history of modern thermodynamics the search for a suitable mathematical model that could describe the phase equilibria of polymers has been a constant. Industrially, the existence of a model to accurately describe the phase equilibria of polymers is of extreme importance. This is true for the manufacturing process where polymer is mixed with solvent (in case of solution polymerization) and monomer. Other substance may sometimes be present as such as initiators of the polymerization reaction but their quantity will not affect the phase equilibria in a significant way. Another process where phase equilibria prediction is needed is in the purification process of the polymer where the solvent and monomer have to be separated from the polymer and recycled to the process. This thesis is another step forward in this search and development of that model.

The main handicap in polymer thermodynamics modeling is the fact that they cannot be built, in mathematical, physical and chemical terms, as other types of molecules, since they differ not only in chemical structure but also in branching, molecular weight, molecular weight distribution, to mention a few. The goal of this work is to model phase equilibria of polymer mixtures by means of several modeling approaches, namely GE models, based in the Universal Quasi Chemical Activity Coefficient (UNIQUAC) model, and equations of state, such as the Statistical Associating Fluid Theory (SAFT), in particular the soft-SAFT and PC-SAFT versions.

In order to gain some grasp of polymer modeling, not only polymers were described, but their precursors, i.e., monomers and oligomers were also modeled. This allowed the understanding of the evolution of the thermodynamic properties with the molecular weight in a given series, such as the *n*-alkane series and ethylene glycol series and the development of correlation schemes which enable the use of the SAFT models in a predictive way.

Special attention was also paid to polymer-solvent associating systems, which was coded and tested for the first time for the soft-SAFT equation of state. The SAFT models showed that they can describe several types of phase equilibria namely the liquid-liquid equilibria with Upper Critical Solution Temperature and/or Lower Critical Solution Temperature, vapor-liquid and gas-liquid equilibria.

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List of Symbols

Roman Letters and abbreviations

a	Activity of the solvent (Figures II.3.1 to II.3.3 and II.3.6)
a	Adjustable energetic parameter (Chapter II)
a, b	Parameter defining the FH parameter as function of temperature (eq. II.3.1)
A	Helmholtz energy
AAD	Average absolute deviation
c	Correction factor introduced in equation II.3.2
EoS	Equation of State
FH	Flory-Huggins
FV	Free volume
G	Energetic parameter for the Wu-NRTL model (Chapter II)
G	Gibbs free energy (Appendix A)
g	Radial distribution function
k_B	Boltzmann constant
LDPE	Low Density Polyethylene
m	Chain length, number of Lennard-Jones segments
Mn	Number molecular weight
Mw	Mass Molecular weight
N	Number of molecules
NP	total number of data points (Table II.3.1)
NRF	Non random factor
NS	Number of data sets (Table II.3.1)
p	correction parameter (eq. II.2.2)
PDMS	Polydimethylsiloxane
PE	Polyethylene
PEG	Poly(ethylene glycol)
PIB	Poly(isobutylene)
PMMA	Poly(methyl methacrylate)
POD	Poly-1-octadecene
PS	Polystyrene
PVAC	Poly(vinyl acetate)

PVAL	Poly(vinyl alcohol)
q	Area parameter
Q	Quadrupole moment ($C \cdot m^2$)
r	Number of segments
R	Real gas constant
T	Temperature
U, u	Energy
V	Molar volume
w	Mass fraction
X	Segment fraction (Chapter II); Fraction of molecules not bonded to a certain site (Chapter III)
x	Molar composition

Greek letters

α	Non-randomness factor
γ	Molar activity coefficient
Δ	difference
ε	soft-SAFT Lennard-Jones energy parameter
η	soft-SAFT binary interaction parameter for size
θ	Area fraction
λ	Energy parameter for the Zafarani-Moatar model
ξ	soft-SAFT binary interaction parameter for energy
σ	Soft-SAFT Lennard-Jones size parameter (segments diameter)
τ	Energetic parameter for the UNIQUAC, sUNIQUAC and Wu-NRTL models
Φ	volume fraction
χ	The Flory parameter
ω	Acentric factor

Subscripts

1	Solvent (Chapter II)
2	Polymer (Chapter II)
c	Critical property
HB	Association related
i	Component *i*

j	Component *j*
LJ	Lennard-Jones
o	Reference
p	polymer
q	Segment relative
r	Reduced property
s	solvent (Chapter II)
seg	segment
w	Van der Waals

Superscripts

assoc	Related to association contributions
chain	Related to chain bonding contributions
comb	combinatorial
comb-fv	Combinatorial free volume
E	Excess
FV	Free volume
ideal	Related with the ideal gas contribution
p	Correcting parameter defined in equation 3
polar	Related to polar moments (di or quadrupolar) contributions
ref	Reference term contributions
res	Residual
total	Total sum of the contributions
α	Site of association

“A verdade de um curso não está no que aí se aprende, mas no que disso sobeja:

o halo que isso transcende e onde podemos achar-nos homens”

Vergilio Ferreira

I. GENERAL INTRODUCTION

I.1. General Context

The term polymer is generally used to describe molecules formed by a repetition of structural units: the monomers. In the polymerization, these monomers react according to different mechanisms depending on the chemistry of the monomer, to form the polymer chain. Polymer chains exhibit a range of properties that illustrate a wide variety of physical chemical principles. From these properties, the molecular weight is by far the one with utmost importance. Contrarily to other molecules of lower molecular weight, the molecular weight of a polymer is a distribution of molecular weights. The statistics of this distribution were studied by Flory (1953) and they depend on the type of reaction and on the type of polymerization. The reaction type can fall into two big groups: addition polymerization and condensation polymerization. The former takes places when the monomer has double bonds, such as the case of styrene, and the reaction is characterized by a fast kinetics leading to more uniform large polymer chains (Carraher, 2006) and as a consequence a narrower molecular weight distribution. In the second one, the monomer involved has multifunctional groups such as diamines, or dicarboxilic acids and since chains of different lengths can grow in the reaction mixture. The polymer formed has a wider molecular weight distribution.

A number of polymerization processes can be used to prepare polymers (Odian, 2004). From these, the most widely used are the solution polymerization, emulsion polymerization and gas phase polymerization. At the end of all these processes one problem arises: the unreacted monomer and the solvent have to be separated from the polymer since they are not desirable in the final product.

In this context, polymer-solvent phase equilibria plays a dominant role in the manufacturing, processing and formulation of polymers. Note that, apart from polymer, unreacted monomer and often solvent which are present in the polymerization reaction, other compounds might also be present,such as initiator, surfactant, etc., but they can usually be neglected in terms of phase equilibria as their amount is usually too small to significantly influence it.

Although polymers are found in a wide spread range of applications, the modeling of phase equilibria of polymers systems still remains a challenging task. The increasing complexity of polymers and polymer systems resulting from new polymerization techniques and the new approaches to their use aggravates this situation. From a past situation where polymers were used in an almost pure state, i. e. few additives were used to improve their chemical and mechanical properties, to the present situation where the polymeric material properties can be tailored to specification by formulation, polymer phase equilibria have increased in complexity but also in importance. The absence of adequate models polymer system properties and phase behavior makes this design procedure a time consuming and costly task that is performed on a trial and error basis with more art and skillful judgment than solid science.

Polymer-solvent solutions usually exhibit fluid phase equilibria of type IV and V according to the classification of Scott and van Konynenburg (1970). The characteristic of these mixtures is the existence of a Lower Critical End Point (LCEP) and an Upper Critical End Point (UCEP). The occurrence of these critical points is due to the large difference of sizes between the two molecules and the difference in compressibility, leading to a large difference in their volatility. The combination of these factors leads to phase split in which three phases may coexist: two liquid phases and one gas phase. In polymer phase equilibria, and particularly in liquid-liquid equilibria, the phase splinting can follow either

or both of the following behaviors: Upper Critical Solutions Temperature (UCST) and Lower Critical Solutions Temperature (LCST). The existence of a LCST is mainly driven by two factors: strong polar integrations, including hydrogen bond, and compressibility effects. In either case the phase splinting comes from the unfavorable entropics of the mixture. The existence of the UCST is driven by unfavorable enthalphics (Sanchez and Panayiotou, 1994).

The usual approach to the modeling of these complex systems falls in two main groups: the free energy models and the Equation of State models. The most successfully used free energy models include Flory-Huggins (Flory, 1942 and Huggins, 1941), Entropic-FV (Elbro et al., 1990, Kontogeorgis et al., 1993) and Freed-FV (Bawendi and Freed, 1988; Dudowicz et a.l, 1990). In spite their success, these models have a few deficiencies, namely they are based on the total randomness of the mixture interactions, not considering the existence of nonrandom interactions such as hydrogen bonding association. The best known corrections for the non randomness are those based on the quasi-chemical theory which lead to the concept of local composition. Such models include NRTL-FH (Chen, 1993) and UNIFAC-FV (Oishi and Prausnitz, 1978) and they usually underestimate this effect. An alternative to this approach, is the use of a chemical theory where the association interactions are modeled as equilibrium chemical reactions where its equilibrium constant is a fitting parameter for the model. The most successful one in terms of its widespread use is the Flory-Huggins model, developed from the lattice fluid theory (Flory, 1942). Its success comes from its mathematical simplicity when compared to equations of state, while the results produced are quite acceptable for several common polymer systems. The free energy models are not reliable for polymers, in the sense that the lattice is incompressible, which is not the behavior of real fluids, as the thermodynamic stability depends on its compressibility. This handicap of the Flory-Huggins model can be minimized by using an equation of state instead of the lattice theory.

On the other hand, there are the equation of state based models such as Sanchez-Lacombe (Sanchez and Lacombe, 1976 and 1978), polymer-Soave-Redlich-Kwong (SRK) (Holderbaum and Gmehling, 1991, Fisher and Gmehling, 1996 and Orbey et al., 1998) and Statistical Association Fluid Theory (SAFT) (Chapman et al., 1989). The Sanchez-

Lacombe Equation of State (EoS) (Sanchez and Lacombe, 1976 and 1978), developed from the lattice fluid theory, has also been quite successful in modeling vapor-liquid equilibria and liquid-liquid equilibria of polymer systems (Naya et al, 2006 and Challa and Visco, 2005). The parameters of the Sanchez-Lacombe equation are found by fitting the saturation pressure and liquid density data for small molecules while PVT data is used for polymers. The polymer-SRK EoS is an extension of the SRK EoS, in which a new UNIFAC based mixing rule is used.

All the models listed before have their strengths and weaknesses and all have been applied successfully in the description of polymer solutions phase equilibria. The choice of a specific model to describe a new polymeric system tends to fall for the most widely used model or the easiest to implement, instead of the model that can give a systematic description of the phase equilibria with physically sound results.

One approach that is rising in popularity, due to its accuracy, is the estimation of thermodynamic properties of polymer solutions by the SAFT EoS. The SAFT equation is based on Wertheim's (TPT1) theory (Wertheim 1984a, 1984b, 1986a and 1986b) and it was later converted into a useful model by Chapman et. al. (1989). The underlying concept behind SAFT is its description of the molecules of interest which has proven to be an advantage for polymers. In its essence the SAFT EoS already considers the molecules as chains of segments, so its application in modeling the phase equilibria of polymer is a natural path to follow. In the SAFT approach, the individual molecules are "constructed" by the addition of different terms: the reference term, the chain term and the association term. The reference term is usually a spherical segment, which can be a Lennard-Jones, a hard sphere and even a square well fluid. These segments are then linked together to make the molecular chains present in the fluid. This concept is the reason why this EoS seems to be appropriate to describe the phase equilibria of long chain molecules, such as polymers. If the molecules are associating (i.e they are able to form hydrogen bonds), an additional term is added to take into account this contribution. Several versions of SAFT have been developed mostly differing in the reference term used (Chapman et al, 1989; Huang and Radosz, 1990; Gil-Villegas et al, 1997; Blas and Vega, 1997 and Gross and Sadowski, 2001). The differences between these versions will be addressed in Chapter III.

The use of the SAFT EoS in modeling the polymer phase equilibria comes from its debut. Huang and Radosz (1990) first presented the modeling of pure polymers with this approach, i. e., only the pure polymer molecular parameters were presented without any modeling of mixtures. Huang and Radosz obtained the molecular parameters of pure polymers by fitting merely to the polymers' densities, as the polymers have no measurable vapor pressure. The first successful modeling of polymer mixtures with the SAFT EoS reported in literature was done by Chen et al (1992), based on the initial suggestion of the previously mentioned work that polymer mixtures could be modeled with the original SAFT EoS. The original SAFT EoS showed very good results in the modeling of mixtures of poly(ethylene-propylene) with some solvents. Following this work, Wu and Chen (1994), Ghonasgi and Chapman (1994) and Koak and Heidemann (1996), successfully applied the SAFT EoS to the modeling of polymer solutions, in particular to the liquid-liquid equilibria presented by these type of systems.

Recently Gross and Sadowski (2001) have developed a variation of the SAFT model (PC-SAFT) in which the reference term is a hard chain fluid instead of a hard sphere fluid. This feature makes this equation very attractive to model polymer phase equilibria since the particular connection between the different segments is already taken into account in the reference term. In fact, at present time PC-SAFT is the most used version of the SAFT EoS for polymers (Gross and Sadowski, 2002 and Sadowski, 2004). In this context, von Solms et al. (2003) recently proposed a simplification in the mixing rules to lower the computing time of phase equilibria calculations with this approach. This model has been applied to a number of system types involving polymer phase equilibria (Kouskoumvekaki et al., 2004a; Kouskoumvekaki et al., 2004b; von Solms et al., 2004 and von Solms et al., 2005).

Taking this into account, it would be interesting develop and to explore the performance of the other SAFT equations in modeling polymer phase equilibria and to compare the obtained results to the ones obtained with PC-SAFT. In particular, the soft-SAFT EoS, developed by Blas and Vega (1997) and improved by Pamiès and Vega (2001), seems to be a promising model for polymer systems. The application of this model would

allow the evaluation of the limits of reliability of the Lennard Jones EoS used in this model for the reference fluid in describing the thermodynamic behavior of polymer systems.

I.2. Scope and Objectives

As it has been stated before, much work has already been done in the modeling of the thermodynamics of polymer systems, especially the phase equilibria. However, a systematic study of the behavior of these systems addressing important issues such as the change in the polymer´s molecular weight, the type of polymer and thus the description of the polymer at the molecular level in order to understand the interactions between polymer-solvent has not yet been done, particularly in the case of the soft-SAFT version, developed by Blas and Vega (1997). This equation of state has been successfully applied to a great number of different systems, from alkanes (Pamiès and Vega, 2001) to perfluoroalkanes (Dias et al., 2004 and 2006) and alcohols (Pamiès, 2003), proving its reliability in the modeling of the phase equilibria of mixtures.

The study of polymer systems by means of excess Gibbs (GE) energy models and Equations of State, namely the SAFT EoS, is a mean to improve not only the understanding of the phenomena present in the physical system itself but also the details of the implementation of the used mathematical models. This thesis will not focus on special cases of polymer phase equilibria, like solutions of copolymers or polymer blends. However, these could be studied just be assuming that the presence of an extra monomer, in the case of copolymers, and it would result in an average of characteristics between those of each polymer formed by each monomer. One only would have to consider the ratio of monomers of each type present. This average of characteristics can easily be incorporated in the SAFT's pure polymer parameters. In the case of polymer blends, the phase equilibria can be modeled as multicomponent a mixture, in the same way it is was done for polydisperse polymers with PC-SAFT (Gross and Sadowski, 2002) and was also accomplished within this work using soft-SAFT, for a bimodal polyethylene as it will be shown in Chapter III.

In the case of the soft-SAFT Equation of State the existence of a fully developed software (Pamiès, 2003) written in *Fortran 77* is an advantage as it can be extended and improved to support, p.e., different versions of the SAFT EoS or corrections to numerical difficulties that arise when dealing with polymer phase equilibria. In fact small corrections had to be made so that the software could calculate phase equilibria of systems involving polymers

With the arguments exposed before, the main purpose of this thesis is to model the phase equilibria of polymer systems, namely polymer-solvent binary mixtures.

Thus, the objectives of this work can be divided as follows:

- Apply a number of GE models to a database of polymer systems and compare their performance,
- Incorporate the PC-SAFT EoS into the existent soft-SAFT phase equilibria calculations software,
- Correct eventual numerical problems that arise in calculation of polymer solutions phase equilibria,
- Improve the capability of the developed software by introducing a generic association calculus procedure for the soft-SAFT and PC-SAFT EoS,
- Use the developed computer program to study the best way to parameterize the pure polymer compounds,
- Calculate the description of the phase equilibria of non-associating polymers, such as polyethylene and polystyrene using the soft-SAFT EoS and comparing it with PC-SAFT EoS,
- Calculate the description the phase equilibria of associating polymers such as polyethylene glycol using the soft-SAFT EoS and comparing it with PC-SAFT EoS

Taking into account the objectives drawn, the thesis will be organized in two different parts. In the first part, the description of the vapor-liquid equilibria of polymer mixtures will be calculated by means of excess Gibbs energy models. Several models will be used to

describe a large database of experimental data and their performance will be compared for the different systems. Along the way a local composition model based on UNIQUAC will be developed. The second part of the thesis will be totally dedicated to model the phase equilibria of polymer systems with the SAFT Equation of State. Different polymers will be modeled, such as polyethylene, polystyrene and polyethylene glycol. Different type of phase equilibria will addressed, namely liquid-liquid equilibria, vapor-liquid equilibria and gas-liquid equilibria.

II. EXCESS GIBBS ENERGY MODELS

II.1. Introduction

The knowledge of the vapor-liquid equilibrium (VLE) of polymer solutions is of great importance for the manufacturing and processing of polymeric materials. In the last few years a wide variety of excess free energy models has been proposed for the activity coefficient of solvents in polymer solutions, including many predictive free volume activity coefficient models such as UNIFAC-FV (Oishi and Prausznitz, 1978) and Entropic-FV (Elbro et al., 1990). A number of models for correlation of VLE and LLE have also been proposed. Chen (1993) developed a segment based local composition model that uses a combination of the Flory-Huggins (FH) expression for the entropy of mixing of molecules and the NRTL to account for the energetic interactions. More recently Wu and coworkers (1996) developed a modified NRTL model to represent the Helmholtz free energy in polymer solutions that was coupled with the Freed Flory-Huggins model (Bawendi and Freed, 1988; Dudowicz et a.l, 1990) (Freed FH) truncated after the first correction to account for entropic contributions. Zafarani-Moattar and Sadeghi (2002) proposed a modification to the non-random factor (NRF) model presented by Haghtalab and Vera (1988) making it usable to account for the energetic interactions on polymer

solutions. In the model developed by Zafarani-Moattar the Freed model is again used to account for the combinatorial contribution.

Although the concept of free volume can be traced back to the work of Flory its first explicit introduction into an activity coefficient model was done by Elbro and coworkers (Elbro, et al., 1990) when they proposed the Entropic free volume for size-asymmetric solutions such as polymer solutions. This model is similar to the Flory-Huggins but free volume fractions are used instead of volume fractions and a better description of the experimental data is achieved. The free volume itself is defined as:

$$V^{FV} = V - V_w \tag{II.1.1}$$

where V_w is the van der Waals volume that represents the hard-core volume of the molecules. According to this model the free volume is the difference between the actual volume occupied by a molecule and its hard-core volume. Kontogeorgis et al. (1994) developed a correction to the Elbro model that accounts for the differences in size between the molecules of solvent and polymer, the p-free volume model.

Using these combinatorial (free volume) and residual terms based on local composition models such as NRTL, NRF and UNIQUAC it is possible to combine them to form distinct models to correlate experimental data. In this work, the capabilities of such models are evaluated.

The advantage of the segment based models over conventional models for correlation of polymer solution experimental data is that, unlike the classical models, they can cover a wide range of polymer molecular weights with a single pair of interaction parameters, what confers them a predictive capability. A segment based UNIQUAC model, sUNIQUAC was here developed following the approach of Wu et al. (1996). This residual term is evaluated along with the other models studied.

The predictive character of the segment-based models will be evaluated for their accuracy and reliability to verify if they can be used outside the range of data used in the correlation of the interaction parameters.

II.2. Thermodynamic models

The activity coefficient models are often expressed as a sum of two terms: a combinatorial-free volume term and a residual term.

$$\ln\gamma_i = \ln\gamma_i^{comb-fv} + \ln\gamma_i^{res} \qquad \text{(II.2.1)}$$

The combinatorial part accounts for the entropic effects mainly related to the size and shape differences of the molecules present in the solution while the residual part accounts for the energetic interactions existent between the solvent and the polymer.

Combinatorial terms

The terms used for the combinatorial part of the model where the Entropic free volume (Elbro et al., 1990), the Freed Flory-Huggins model (Bawendi and Freed, 1988; Dudowicz et al., 1990) and the p-free volume model (Coutinho et al., 1995). Numerous comparisons have established the advantages of the free volume terms proposed as well as their limitations (Coutinho et al., 1995; Polyzou et al, 1999; Kouskoumvekaki et al., 2002). The Freed FH although it does not account for free volume effects was studied since it has been adopted in recent polymer models (Wu et al., 1996; Zaffarani-Moattar and Sadeghi, 2002).

Both the Entropic free volume and the p-free volume terms are based in the Flory-Huggins model with the difference that they use free volume fractions instead of volume fractions. The free volume is defined in Eq. II.1.1.

In the p-free volume model a correction factor, p, defined as:

$$p = 1 - \frac{V_1}{V_2} \qquad \text{(II.2.2)}$$

was introduced into the original Entropic free volume. The free volume for this model is thus defined as:

$$V^{FV} = \left(V - V_w\right)^p \qquad \text{(II.2.3)}$$

For both models, Entropic free volume and p-free volume, the free volume fraction is expressed as:

$$\varphi_i^{FV} = \frac{x_i V_i^{FV}}{\sum_j x_j V_j^{FV}} \tag{II.2.4}$$

The combinatorial term based in these free volume fractions can be described as:

$$\ln \gamma_1^{comb-fv} = \ln\left(\frac{\varphi_1^{FV}}{x_1}\right) + 1 - \frac{\varphi_1^{FV}}{x_1} \tag{II.2.5}$$

The Freed *Flory-Huggins* combinatorial term is the exact solution for the Flory-Huggins lattice theory. It is expressed as a polynomial expansion in powers of a non-randomness factor, similar to the existent in NRTL. Freed only used the first order correction:

$$\ln \gamma_1^{comb} = \ln\left(\frac{\varphi_1}{x_1}\right) + \left(1 - \frac{r_1}{r_2}\right)\varphi_2 + \alpha\left(\frac{1}{r_1} - \frac{1}{r_2}\right)^2 \varphi_2^2 \tag{II.2.6}$$

This combinatorial term, unlike the terms described previously, does not take into account the free volume contributions to the free energy.

Residual terms

The residual terms studied are the original UNIQUAC (Abrams and Prausnitz, 1975) and three segment based local composition models: NRTL as proposed by Wu et al (1996), NRF (Zaffarani-Moattar and Sadeghi, 2002), and sUNIQUAC, a residual term based on UNIQUAC here developed. All these terms have two interaction parameters to be fitted to experimental data.

The NRF model used is a segment-based modification of the original NRF model made by Zafarani-Moattar and Sadeghi (2002) and can be described as:

$$\ln \gamma_1^{res} = \frac{x_1^2 \lambda_1 + 2 r_2 x_2 x_1 \lambda_1 + r_2 x_2^2 \lambda_{seg}}{\left(x_1 + r_2 x_2\right)^2} - \frac{r_2 x_2^2 \lambda_{seg} e^{-\alpha \lambda_{seg}}}{\left(x_1 + x_2 e^{-\alpha \lambda_{seg}}\right)^2} - \frac{x_1^2 \lambda_1 + 2 x_1 x_2 \lambda_1 e^{-\alpha \lambda_1}}{\left(x_1 + x_2 e^{-\alpha \lambda_1}\right)^2} \tag{II.2.7}$$

Being λ_1 and λ_{seg} the energetic interaction parameters for the solvent and polymer segments respectively. Following Wu et al. (1996), Zafarani-Moattar defined these parameters as functions of temperature:

$$\lambda_1 = a_1 \frac{T_0}{T} \tag{II.2.8}$$

$$\lambda_{seg} = a_{seg} \frac{T_0}{T} \tag{II.2.9}$$

The parameters, a_1 and a_{seg} are fitted to experimental data and are temperature independent.

The model proposed by Wu and his coworkers (Wu et al., 1996) is a segment-based modification of the original NRTL model with the following form:

$$\ln \lambda_1^{res} = q_1 X_2^2 \left(\frac{\tau_{21} G_{21}^2}{\left(X_1 + X_2 G_{21}\right)^2} + \frac{\tau_{12} G_{12}}{\left(X_2 + X_1 G_{12}\right)^2} \right) \tag{II.2.10}$$

In which the energetic terms are expressed as in the NRTL model.

$$\tau_{ij} = e^{\frac{a_{ij}}{RT}} \tag{II.2.11}$$

$$G_{ij} = e^{-\alpha \tau_{ij}} \tag{II.2.12}$$

The parameters a_{ij} are fitted to the experimental data. The compositions used in the model are not the molar compositions but the segment compositions defined as

$$X_i = \frac{N_i q_i}{N_q} \tag{II.2.13}$$

$$N_q = \sum_i N_i q_i \tag{II.2.14}$$

With N_i being the number of molecules of component *i* and N_q is the total number of segments present in the solution mixture. The q_i is the actual number of segments for species *i* and is usually related to r_i by:

$$q_i = r_i \left(1 - 2\alpha \left(1 - \frac{1}{r_i} \right) \right) \tag{II.2.15}$$

where α is the factor non-randomness defined in the same way as in the original NRTL model.

The value of r_i is taken as unity for the solvent and for the polymer it is obtained from the ratio between the polymer and solvent molar volumes.

The original UNIQUAC model was also studied as it generally provides a good description of the experimental VLE data. Its residual part for a binary mixture is presented below.

$$\ln\gamma_1^{res} = -q_1 \ln\left(\theta_1 + \theta_2\tau_{21}\right) + \theta_2 q_1\left(\frac{\tau_{21}}{\theta_1+\theta_2\tau_{21}} - \frac{\tau_{12}}{\theta_2+\theta_1\tau_{12}}\right) \tag{II.2.16}$$

The parameters τ_{ij} and θ_i are defined as:

$$\tau_{ij} = e^{\frac{-a_{ij}}{T}} \tag{II.2.17}$$

$$\theta_i = \frac{x_1 q_i}{\sum_j x_j q_j} \tag{II.2.18}$$

With the a_{ij} being the energetic parameters to be fitted to the experimental data.

The sUNIQUAC model was derived following the approach of Wu and co-workers for the development of a segment based model. In this model the segment composition is defined in the same way as in the Wu-NRTL model, and the definitions of q_i and r_i also apply to this model. The residual term has the following form:

$$\ln\gamma_1^{res} = -q_1 \ln\left(X_1 + X_2\tau_{21}\right) + X_2 q_1\left(\frac{\tau_{21}}{X_1+X_2\tau_{21}} - \frac{\tau_{12}}{X_2+X_1\tau_{12}}\right) \tag{II.2.19}$$

with the X_i being the segment fraction as defined above in Eqs. (II.2.13)-(II.2.14), and τ_{ij} as defined for the original UNIQUAC. A detailed derivation of this model is presented in Appendix A.

II.3. Results and discussion

The coupling of the various combinatorial (free volume) and residual terms presented above leads to different activity coefficient models some of which have been previously proposed in the literature and others which are here studied for the first time. These models

have been tested for their performance in the correlation of experimental VLE data. A total of 70 experimental data sets of polymer-solution systems from the literature (Flory and Daoust, 1957; Bawn and Patel, 1956; Baker et al., 1962; Tait and Abushihada, 1977; Dolch et al., 1984; Ashworth and Price, 1986a; Ashworth and Price, 1986b; Kim et al., 1998; Ashworth et al., 1984; Kuwahara et al., 1969; Noda, et al., 1984; Baughan, 1948; Saeki et al., 1981; Bawn and Wajid, 1956; Scholte, 1970a; Scholte, 1970b; Krigbaum and Geymer, 1959; Hocker and Flory, 1971; Flory and Hocker, 1971; Bawn et al., 1950; Iwai and Arai, 1989; Cornelissen et al., 1963; Tait and Livesey, 1970; Kokes et al., 1953; Herskowitz and Gottlieb, 1985; Ninni et al., 1999; Vink, 1971; Sakurada et al., 1959 and Castro et al., 1987) were used in this work to compare the performance of all models studied. The source of the experimental data used is reported in Table II.3.1. All the models studied have two interaction energy parameters to be fitted to the experimental data. For the models with a non-randomness parameter (α), its value was fixed to 0.4, a typical value for this parameter, to keep the number of adjustable parameters to two.

Table II.3.1: Experimental data used on this work and the deviations (AAD%) obtained for Flory Huggins and the segment-based models

System	Mn_2 (range)	T (K) (range)	NS	NP	Literature Source	Flory-Huggins	p-FV / Wu-NRTL	p-FV / NRF	p-FV / sUNIQUAC
PIB/cyclohexane	90000-100000	281.15-338.15	2	50	Flory and Daoust, 1957; Bawn and Patel, 1956	0.61	0.60	**0.44**	0.57
PIB/benzene	45000-84000	297.75-338.15	2	62	Flory and Daoust, 1957; Bawn and Patel, 1956	1.73	1.56	**1.18**	1.26
PIB/n-pentane	1170-8400	297.75-338.15	1	96	Baker et al., 1962	0.73	0.44	0.46	**0.35**
PDMS/Benzene	1140-89000	298.15-313.15	8	103	Tait and Abushihada, 1977; Dolch et al., 1984; Ashworth and Price, 1986a	0.85	0.78	0.77	**0.65**
PDMS/Chloroform	89000	303	1	7	Ashworth and Price, 1986b	0.20	0.36	0.14	**0.06**
PDMS/n-hexane	6650-26000	303.15	2	24	Kim et al., 1998	1.37	0.64	**0.49**	1.07
PDMS/n-pentane	89000	303.15	1	15	Ashworth et al., 1984	**0.16**	0.29	0.17	**0.16**
PDMS/cyclohexane	12000-89000	293.15-303	2	40	Ashworth et al., 1984; Kuwahara et al., 1969	**0.20**	0.24	**0.20**	**0.20**
PS/benzene	63000-600000	288.15-333.15	3	48	Noda, et al., 1984; Baughan, 1948; Saeki et al., 1981	1.84	**0.84**	1.81	1.17
PS/n-bytil acetate	500000	293.15	1	9	Baughan, 1948	3.69	**2.10**	2.37	**2.10**

System	Mn_2 (range)	T (K) (range)	NS	NP	Literature Source	Flory-Huggins	p-FV / Wu-NRTL	p-FV / NRF	p-FV / sUNIQUAC
PS/carbon tetrachloride	500000-600000	293.15-296.65	2	18	Baughan, 1948; Saeki et al., 1981	0.69	0.72	**0.65**	0.68
PS/Chloroform	90000-600000	296.65-323.15	3	32	Saeki et al., 1981; Bawn and Wajid, 1956	2.12	**1.19**	2.06	1.44
PS/cyclohexane	49000-500000	293.15-338.15	8	125	Baughan, 1948; Saeki et al., 1981 Scholte, 1970a; Scholte, 1970b; Krigbaum and Geymer, 1959	0.83	**0.26**	0.36	0.27
PS/diethyl ketone	200000-500000	293.15	2	18	Baughan, 1948	8.03	**2.10**	2.95	2.16
PS/1,4 dioxane	10300-500000	293.15-323.15	2	14	Tait and Abushihada, 1977; Baughan, 1948	5.44	2.02	3.73	**2.01**
PS/ehtyl benzene	97200	283.15-333.15	1	14	Hocker and Flory, 1971	0.05	0.05	0.05	**0.02**
PS/ethyl methyl kentone	10300-290000	283.15-343.15	3	37	Tait and Abushihada, 1977; Flory and Hocker, 1971; Bawn et al., 1950	1.59	1.20	1.02	**0.99**
PS/acetone	15700	298.15-333.15	1	16	Bawn and Wajid, 1956	4.85	0.69	3.02	**0.37**
PS/ n-nonane	53700	403.15-448.15	1	16	Iwai and Arai, 1989	**2.94**	5.14	3.28	4.02
PS/n-propyl acetate	290000	298.15-343.15	1	21	Bawn and Wajid, 1956	1.51	1.59	**0.91**	1.52

System	Mn_2 (range)	T (K) (range)	NS	NP	Literature Source	Flory-Huggins	p-FV / Wu-NRTL	p-FV / NRF	p-FV / sUNIQUAC
PS/toluene	7500-600000	293.15-353.15	8	148	Tait and Abushihada, 1977; Baughan, 1948; Saeki et al., 1981; Scholte, 1970a; Scholte, 1970b; Bawn et al., 1950; Cornelissen et al. , 1963	0.72	0.62	0.74	**0.39**
POD/Toluene	94900-220800	303.15	3	31	Tait and Livesey, 1970	4.94	**1.56**	2.47	2.37
PVAC/acetone	170000	303.15-323.15	1	15	Kokes et al., 1953	3.87	**1.44**	6.22	3.27
PEG/water	200-43500	293.1-333.1	16	200	Herskowitz and Gottlieb, 1985; Ninni et al., 1999; Vink, 1971	3.59	1.49	1.73	**1.16**
PVAL/water	14800-67400	303.15	2	10	Sakurada et al., 1959	11.66	**2.08**	2.35	2.50
LDPE/n-pentane	24900	263.15-308.15	1	70	Castro et al., 1987	**3.12**	6.69	3.15	4.21
LDPE/n-heptane	24900	288.15-318.15	1	34	Castro et al., 1987	4.92	8.51	**4.20**	6.40
PMMA/toluene	19770	321.65	1	8	Tait and Abushihada, 1977	1.48	1.64	1.45	**1.39**
					%AAD (NS weighted average)	2.45	1.25	1.43	**1.14**

II.3.1. Correlation

The results obtained by the various models were compared to the results obtained with a two parameter Flory-Huggins model. This is a standard model for the correlation of phase behavior of polymer solutions, therefore being an adequate model to be used to evaluate the performance of new models. The χ parameter of the residual term of Flory-Huggins was defined using a linear dependence on the inverse of the temperature (Kontogeorgis et al., 1994):

$$\chi = a + \frac{b}{T} \qquad \text{(II.3.1)}$$

The deviations obtained using Flory-Huggins and the segment-based models for the correlation of the experimental data are reported on Table II.3.1 for each individual system studied. Average deviations for all the models studied are reported in Table II.3.2 as percent improvement over the Flory-Huggins model defined as (AAD_{FH}%/AAD%-1)x100. These results show the advantage of the p-free volume over the other combinatorial free volume terms studied. Coupled with both the NRF or sUNIQUAC residual terms, it produces a description of the data that is consistently superior to the other combinatorial terms studied.

Table II.3.2: Percent improvement [(AADFH/AAD-1)x100] achieved by the models studied over the two-parameter Flory-Huggins model

	Wu-NRTL	**NRF**	**UNIQUAC**	**sUNIQUAC**
Freed FH	-	44.4	-	104.4
p-free volume	96.0	70.8	139.8	114.7
Entropic free volume	-	51.3	-	89.3

The p-free volume term, however, can only be applied to binary systems since there is no way to extend its validity to multicomponent systems. For multicomponent systems the use of the combinatorial free volume term recently proposed by Kouskoumvekaki et al. (2002) is suggested. On their work the authors state that the volume accessible to a

molecule is smaller than the volume admitted by the Entropic free volume definition. Instead a volume larger than the molecules' hard-core is effectively inaccessible to the solvent and the free volume is defined as:

$$V^{FV} = V - c\,V_w \qquad \text{(II.3.2)}$$

where the constant *c* has, according to the authors, the optimum value of 1.2 for the majority of systems. This combinatorial term seems to behave closely to the p-free volume with the advantage of an easy extension to multicomponent systems.

Concerning the residual term the results reported in Table II.3.2 clearly show the advantage of the UNIQUAC based models. The model that this comparison indicates to be recommended for VLE correlation would be a combination of the UNIQUAC residual term with a p-free volume combinatorial term. With an AAD% of about 1% this model would provide a description of the data within their experimental uncertainty.

It should be kept on mind that the possibility of using a third adjusting parameter offered by the NRF or NRTL based models can be of importance in the description of LLE. For the correlation of VLE data the UNIQUAC-p-free volume model seems, however, to be more adequate.

A comparison with the performance of a predictive model was also carried. The UNIFAC-FV model (Oishi and Prausnitz, 1978) was used and a global AAD% of circa 5% was obtained. This is a deviation that although acceptable for many purposes is much superior to the uncertainty of the experimental data. Deviations with UNIFAC-FV are particularly large for systems where one of the components is highly polar such as PDMS / Benzene (Ashworth and Price, 1986a) (Mn_2 = 3850) (AAD% = 24 %) or PEG / water (Sakurada et al., 1959) (Mn_2 = 43500) (AAD% = 55 %).

The behavior of the models on the correlation of experimental data is shown in Figures II.3.1 and II.3.2 for the systems PS/1,4-Dioxane (Tait and Abushihada, 1977) and PEG/Water (Herskowitz and Gottlieb, 1985).

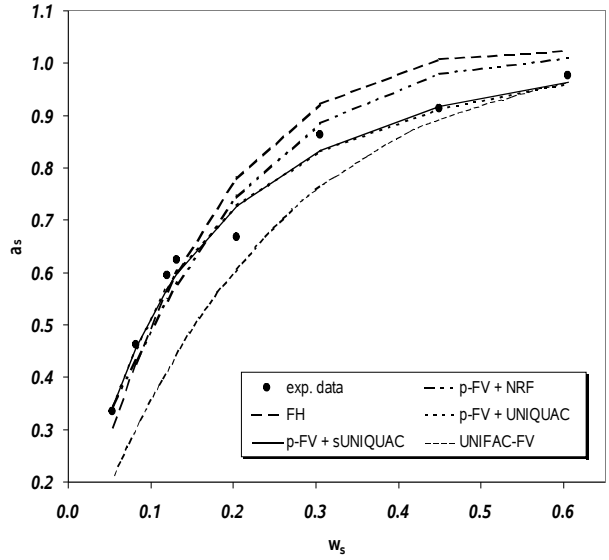

Figure II.3.1: Experimental and correlated solvent activities for the PS/1,4-Dioxane system. (Mn_2 = 10300, T = 323.15 K) (Tait and Abushihada, 1977) (p-FV-UNIQUAC: a_{12}=-0.482; a_{21} = 1.000) (p-FV+NRF: a_1 = -0.646; a_{seg} = -2.106) (p-FV+sUNIQUAC: a_{12} = 0.112; a_{21} = 0.951) (FH: a = 6.261; b = 8.274)

Figure II.3.1 shows the deviations of the UNIFAC-FV model to increase with the polymer concentration. Flory-Huggins also displays some difficulty in describing the experimental behavior being unable to provide the adequate trend of the data. Moreover the results for the NRF based model presented in Figure II.3.2 also show a strange behavior at high polymer concentrations, which is discussed below. Figure II.3.2 also shows the difficulty of the Flory-Huggins and NRF models to describe the experimental data for polar systems.

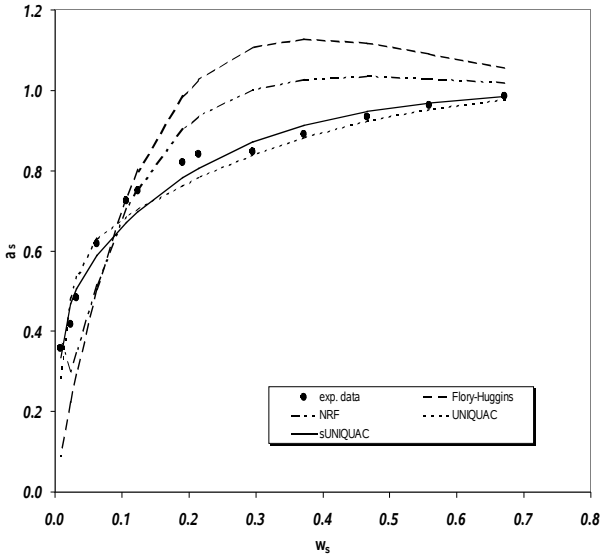

Figure II.3.2: Experimental and correlated solvents activities for the PEG/water system (Herskowitz and Gottlieb, 1985) using the p-FV model as combinatorial term (Mn_2 = 6000; T = 313.15 K) (FH: a = 1.852; b = -1.216) (NRF: a_1 = 0.152; a_{seg} = -0.041) (UNIQUAC: a_{12} = -0.961; a_{21} = 1.831) (sUNIQUAC: a_{12} = 1.045; a_{21} = 2.390)

II.3.2. Prediction

More interesting than the capacity of a model to correlate a set of experimental data it is its predictive capability. Once the energetic parameters have been fitted to experimental data it should be possible to use them to predict the activity coefficient of the solvent, for the same polymer/solvent system for any polymer molecular weight. The predictive capacities of the segment based residual terms used in this work, Wu-NRTL, NRF and sUNIQUAC, were investigated. A comparison with a purely predictive model such as UNIFAC-FV is presented.

For the segment based residual terms the energetic parameters do not account for the energetic interactions between the molecules of the solvent and of the polymer but the interactions between the solvent, taken as the unitary segment, and the polymer segments. The polymer is considered to be composed by a number of segments proportional to the polymer chain length. Taking r_1 as unity and estimating r_2 from the following relation it is possible to count the number of segments in the polymer:

$$r_2 = \frac{V_2}{V_1} \qquad \text{(II.3.3)}$$

To compare the performances of the activity coefficient models obtained coupling the segment based residual terms with the p-free volume, systems for which data on a broad range of molecular weights was available were used. The systems chosen were PS/cyclohexane (Baughan, 1948; Saeki et al., 1981; Scholte, 1970a; Scholte, 1970b and Krigbaum and Geymer, 1959), PS/toluene (Tait and Abushihada, 1977; Baughan, 1948; Saeki et al., 1981; Scholte, 1970a; Scholte, 1970b; Bawn et al., 1950 and Cornelissen et al., 1963), PDMS/benzene (Tait and Abushihada, 1977; Dolch et al., 1984 and Ashworth and Price, 1986a) and PEG/water (Herskowitz and Gottlieb, 1985; Ninni et al., 1999 and Vink, 1971).

To investigate the predictive performance of these models, the energetic interaction parameters were fitted to the data at a single molecular weight and used to predict the activities for the remaining data at other polymer molecular weights. The results obtained are reported in Tables II.3.3 to II.3.6. In general the models investigated provide a good predictive description of the systems studied.

Table II.3.3: Average absolute deviations (%) obtained with predictive models studied as function of the polymer molecular weight for the PS / cyclohexane system (Baughan, 1948; Saeki et al., 1981; Scholte, 1970a; Scholte, 1970b and Krigbaum and Geymer, 1959). The interaction parameters presented were fitted to the data on the top row.

Mn_2	NRF	Wu-NRTL	sUNIQUAC	UNIFAC-FV
154000	0.237	0.041	0.027	2.49
49000	0.145	0.008	0.023	0.03
72000	0.164	0.036	0.030	0.06
110000	23.552	0.497	2.436	17.75
435000	0.021	0.003	0.003	0.02
440000	2.820	1.415	0.980	10.70
500000	1.732	1.509	1.828	7.34
a_{12}	-0.476	2.909	0.540	-
a_{21}	-3.750	-0.249	0.452	-

Table II.3.4: Average absolute deviations (%) obtained with predictive models studied as function of the polymer molecular weight for the PS / toluene system (Tait and Abushihada, 1977; Baughan, 1948; Saeki et al., 1981; Scholte, 1970a; Scholte, 1970b; Bawn et al., 1950 and Cornelissen et al., 1963). The interaction parameters presented were fitted to the data on the top row.

Mn_2	NRF	Wu-NRTL	sUNIQUAC	UNIFAC-FV
7500	0.680	1.253	0.611	6.299
10300	0.542	0.872	0.533	11.131
49000	0.067	0.169	0.055	0.379
154000	1.889	1.738	1.930	2.397
200000	2.146	2.774	2.061	11.178
290000	1.431	1.823	1.354	8.497
435000	0.025	0.046	0.022	0.084
600000	5.306	5.108	5.349	6.932
a_{12}	-0.158	1.635	0.653	-
a_{21}	-0.022	-0.782	-0.323	-

Table II.3.5: Average absolute deviations (%) obtained with predictive models studied as function of the polymer molecular weight for the PDMS / benzene system (Tait and Abushihada, 1977; Dolch et al., 1984 and Ashworth and Price, 1986a). The interaction parameters presented were fitted to the data on the top row.

Mn_2	NRF	Wu-NRTL	sUNIQUAC	UNIFAC-FV
6650	0.369	0.305	0.074	12.617
1140	4.506	7.948	8.18	5.476
1540	11.086	12.583	13.08	1.363
3350	2.725	4.235	3.923	11.773
4170	9.073	6.119	8.388	2.946
15650	2.316	3.381	3.211	13.421
26000	3.517	4.861	4.734	14.318
89000	4.818	5.959	5.665	14.095
a_{12}	-0.603	2.392	0.903	-
a_{21}	-0.010	-0.336	-0.019	-

Table II.3.6: Average absolute deviations (%) obtained with predictive models studied as function of the polymer molecular weight for the PEG / water system (Herskowitz and Gottlieb, 1985; Ninni et al., 1999 and Vink, 1971). The interaction parameters presented were fitted to the data on the top row.

Mn_2	NRF	Wu-NRTL	sUNIQUAC	UNIFAC-FV
200	2.115	1.993	1.610	35.0
400	1.355	2.196	1.350	22.1
600	4.398	4.658	4.011	12.6
1450	0.733	1.853	1.046	12.1
1500	9.442	7.276	7.117	27.8
3350	0.249	0.695	0.321	5.4
6000	1.500	0.586	0.738	14.4
8000	0.284	0.635	0.282	5.4
10000	0.282	0.658	0.304	5.4
20000	0.354	0.566	0.286	5.3
43500	0.046	0.050	0.048	54.9
a_{12}	0.148	-1.057	-0.990	-
a_{21}	-0.034	2.054	2.003	-

Figure II.3.3 shows the predictive behavior of the three models for the PS/toluene (Bawn et al., 1950) with a polymer molecular weight of 290000. The interaction parameters used have been fitted to data for a polymer molecular weight of 10300 (Tait and Abushihada, 1977). The results of the three models are very similar and provide an excellent description of the experimental data.

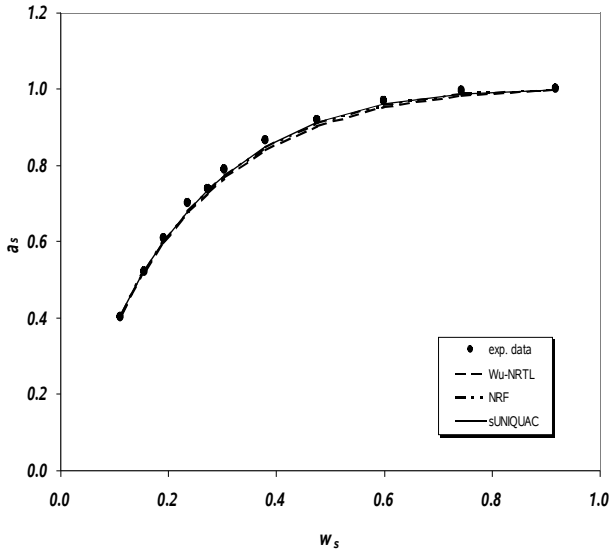

Figure II.3.3: Prediction for the PS / toluene system (Mn_2 = 290000) (Bawn et al., 1950) when using p-FV as combinatorial term and NRF (a_1 = -0.158; a_{seg} = -0.022), Wu-NRTL (a_{12} = 1.635; a_{21} = -0.782) and sUNIQUAC (a_{12} = 0.653; a_{21} = -0.323) as residual terms. The energy parameters were obtained by correlation of the PS/toluene system with Mn_2 = 10300 (Tait and Abushihada, 1977).

Considering that the range of the polymer's molecular weight covers two orders of magnitude the performance of the models is surprisingly good. As shown in Tables II.3.3 to II.3.6 there is no degradation of the predictions with increasing molecular weight, in fact, no relation of the error with the molecular weight is observed. The interaction parameters presented on the Tables II.3.3 to II.3.6 have been fitted to the system presented in the first row and were used for all the other molecular weights.

The models used to predict the solvent's activity can in fact predict changes with the molecular weight of the polymer present in the system. This can be clearly seen in Figures II.3.4 and II.3.5 where the logarithm of the activity coefficient is plotted for several molecular weights, represented by the number of segments (*r*). The study is made in two different systems: PEG/water and PDMS/benzene. These systems account for two major types of interaction polymer/solvent. In the former the interactions are of the type polar and the in the latter they are of type non-polar. Comparing Figures II.3.4 and II.3.5 the model shown not only can predict changes with the polymer's molecular weight but also the behavior of a specific system, that is, for the PEG/water system (Figure II.3.4) the activity coefficient is independent of the molecular weight for *r* values higher than 30 and with

negative deviations from Raoult's law and for the PDMS / benzene system the activity coefficient starts to be independent of the polymer's molecular weight for values of *r* higher than 100 and shows both positive and negative deviations from Raoult's law.

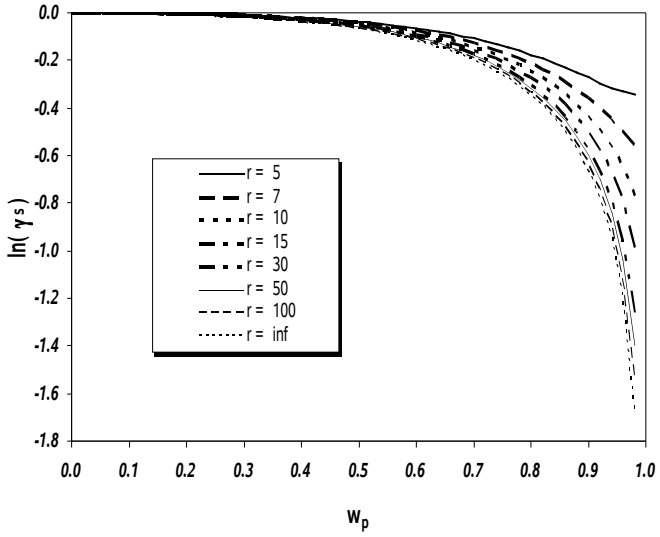

Figure II.3.4: Dependence of the activity coefficient with the polymer's molecular weight for the PEG / water system at 298 K using the sUNIQUAC model (a_{12} = -0.990; a_{21} = 2.003)

The performance of the NRF model is generally somewhat inferior to the other two models and it was found that it presents a strange and unexpected behavior that is reflected on large deviation for the PS/ Cyclohexane system with a molecular weight of 110000 reported on Table II.3.3.

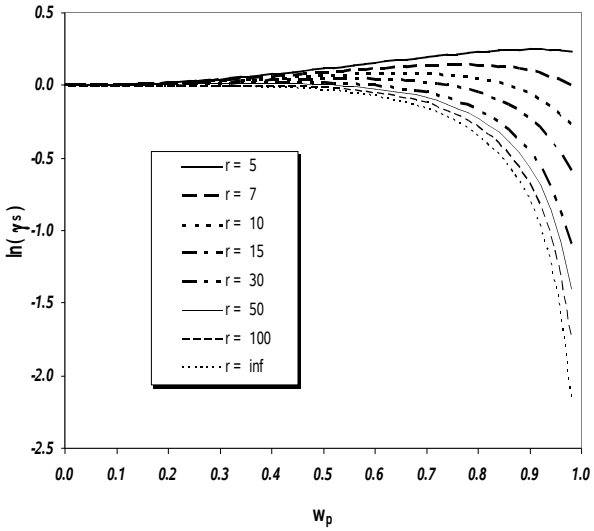

Figure II.3.5: Dependence of the activity coefficient with the polymer's molecular weight for the PDMS / benzene system at 298 K using the sUNIQUAC model (a_{12} = 0.903; a_{21} = -0.019)

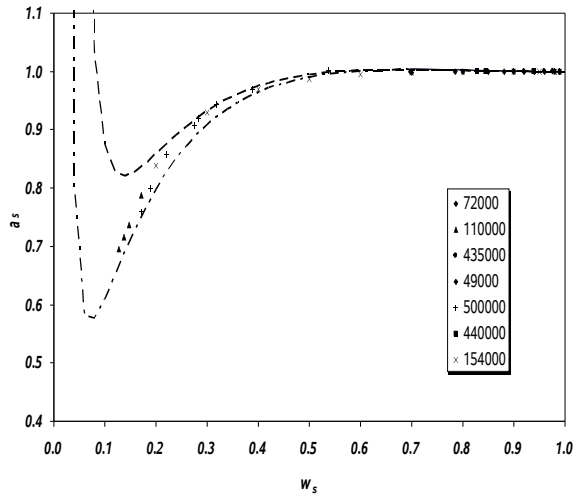

Figure II.3.6: Behavior of the p-free volume + NRF model for the PS / cyclohexane system (a_1 = -0.477; a_{seg} = -3.751): correlation (– –) (Mn_2 = 154000), prediction: (···) (Mn_2 = 110000), (– · –) (Mn_2 = 500000)

Although the overall performance of NRF is acceptable in what concerns the accuracy of the experimental data description, it was found that it displays an odd behavior for high polymer concentrations that make it unreliable for extrapolation in concentration or molecular weight outside the range of experimental data used for parameter fitting. For these concentrations instead of a regular and smooth behavior NRF displays a minimum

followed by a sharp increase on the predicted activities as shown in Figure II.3.6. This behavior, which was already observed in Figure II.3.2, is physically unsound and makes this model unreliable for extrapolation. Its use should be restricted to within the range of experimental data used in the parameter fitting thus limiting its application to the correlation of experimental data.

II.4. Conclusions

A comparison of a number of two parameters activity coefficient models for the correlation of VLE data for polymer systems was performed. The models studied were obtained coupling the best and better-known combinatorial (free volume) terms with residual terms based on the local composition models NRF, NRTL and UNIQUAC. Some of the studied systems had already been proposed in the literature while others are here used for the first time. In particular the sUNIQUAC was developed here and it seems to be a quite good residual term for describing VLE of polymer solutions.

The comparison performed indicates the advantage of the segment-based models derived from the NRTL and UNIQUAC formalisms. These models are able to produce the best correlations for the VLE experimental data and also present the capacity to describe the VLE behavior of a broad range of polymer weights using a single pair of interaction parameters, when coupled to a good combinatorial free volume term, such as the p-free volume used here or other equivalent.

The results obtained also indicate that NRF based models display a physical unsound behavior and while they may be adequately used for the correlation of VLE data the extrapolation of this data to higher polymer concentration or molecular weights other than the used in the correlation is not advisable.

III. THE STATISTICAL ASSOCIATING FLUID THEORY

III.1. Introduction

Despite the wide use of the Free Volume based Excess Gibbs energy models in the description of the phase equilibria of polymer mixtures, they still present a few limitations as already mentioned in Chapter I: they do not consider the compressibility of the mixture fluids, and this is particularly important in liquid-liquid phase equilibria, and they do not account explicitly for nonrandom interactions such as hydrogen bonds without the use of an additional theory. Another limitation of the GE based models is the pressure range: they are not applicable at very high pressures. The solution to these limitations is use an Equation of State based model.

Much effort has been devoted in recent years towards the development of molecular based equations of state, mainly due to their ability to predict accurately the behavior of complex fluids and/or extreme conditions, for which other classical methods fail. Among the equations of state, the Statistical Associating Fluid Theory (SAFT) (Chapman et al., 1988; Chapman et al., 1990 and Huang and Radosz, 1990) is becoming very popular in academic and industrial environments, due to its success in predicting the behavior of a

wide variety of industrial relevant mixtures. This theory has generated a series of different versions of what are now known as SAFT-type equations, based on Wertheim's first-order thermodynamic perturbation theory (TPT1) (Wertheim, 1984a, 1984b, 1986a and 1986b). The most used version of the SAFT equation is the one developed by Huang and Radosz (1990). These authors parameterized the equation for several pure fluids and mixtures showing its applicability for real engineering applications from its development. Although the SAFT family of equations has some known limitations and some of the fitted parameters lack of physical meaning, it is straightforward to implement and relatively easy to use. Other recent, more refined, modifications of SAFT include the soft-SAFT equation of Vega and co-workers (Blas and Vega, 1997; Blas and Vega, 1998 and Pamiès and Vega, 2001), the SAFT-VR equation of Jackson and co-workers (Gil-Villegas et al., 1997) and the PC-SAFT equation of Sadowski and co-workers (Gross and Sadowski, 2001). All SAFT-type equations use Wertheim's theory for the chain and association term, while they differ mainly in the reference term. A detailed discussion on the success and limitations of SAFT equations, improvements and applications can be found in two excellent reviews published on the subject (Müller and Gubbins, 2001 and Economou, 2002).

The general expression for SAFT is given in terms of the residual Helmholtz energy, A^{res}, defined as the molar Helmholtz energy of the fluid relative to that of an ideal gas at the same temperature and density. This residual Helmholtz energy can be obtained as the sum of the independent microscopic contributions. For the systems investigated in this work, the general expression of the SAFT equation is:

$$A^{res} = A^{total} - A^{ideal} = A^{ref} + A^{chain} + A^{assoc} + A^{polar} \qquad \text{(III.1.1)}$$

In order to apply the soft-SAFT equation, a molecular model for each of the compounds integrating the mixture needs to be proposed. The molecular parameters to be obtained by fitting to experimental data are: m, the chain length, σ, the segment size, ε, the dispersive energy of interaction, and ε_{HB} and k_{HB}, the energy and volume of association per site, respectively. In Figure III.1.1 it is shown an hypothetical model of an associating molecule as modeled in the SAFT approach.

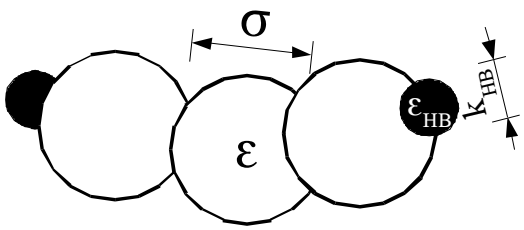

Figure III.1.1: Molecule model within the SAFT approach

The Helmholtz free energy of a pure ideal fluid, A^{ideal}, is given by:

$$A^{ideal} = RT\,(\ln\rho - 1) \tag{III.1.2}$$

The reference term, A^{ref}, usually describes the properties of the individual units that compose the chain. Different versions of SAFT use different terms for the reference fluid, such as hard spheres with a perturbative term to take into account the dispersive forces (Chapman et al., 1988), square-well spheres of variable range (Gil-Vellegas et al., 1997), Lennard-Jones spheres (LJ) (Blas and Vega, 1998 and Johnson et al. 1994) or perturbed hard-chains (Gross and Sadowski, 2001).

The SAFT version on which this work is focused, the soft-SAFT, uses the Lennard-Jones EoS that was developed by Johnson et al., (1993) to model the reference fluid. It consists of a modified Benedict-Webb-Rubbin EoS to which simulation data was fitted and the equation parameters were determined. The equation is extended to mixtures using the van der Waals one-fluid theory (vdW-1f) (Hansen and McDonald, 1990). The corresponding expressions for the mixing rules for the size and energy parameter are:

$$\sigma^3 = \frac{\sum_i \sum_j x_i x_j m_i m_j \sigma_{ij}^3}{\left(\sum_i x_i m_i\right)^2} \tag{III.1.3}$$

$$\varepsilon\sigma^3 = \frac{\sum_i \sum_j x_i x_j m_i m_j \varepsilon_{ij} \sigma_{ij}^3}{\left(\sum_i x_i m_i\right)^2} \tag{III.1.4}$$

For the determination of unlike parameters, the generalized Lorentz-Berthelot combining rules are employed:

$$\sigma_{ij}=\eta_{ij}\frac{\sigma_{ii}+\sigma_{jj}}{2} \tag{III.1.5}$$

$$\varepsilon_{ij}=\xi_{ij}\sqrt{\varepsilon_{ii}\varepsilon_{jj}} \tag{III.1.6}$$

where η_{ij} and ξ_{ij} are the binary adjustable parameters for the species *i* and *j*. As shown in the previous expressions, it is possible to explicitly separate deviations in molecular size form deviations in energy, by fitting both. It is also possible to account for all deviations with a single binary parameter. The advantage would be that there is only one binary parameter to fit, and the disadvantage that this single parameter would account for both deviations, resulting in larger deviations from unity, the ideal value.

The chain term, A^{chain}, accounts for the energy of formation of chains from units of the reference fluid. This term is obtained taking the limit of complete bonding in Wertheim's TPT1 and it is formally identical in all versions of SAFT. The Helmholtz free energy due to the formation of chains from m_i spherical segments can be written as

$$A^{chain}=RT\sum_i x_i\left(1-m_i\right)\ln g_{LJ} \tag{III.1.7}$$

where $R=k_B N_A$ is the ideal gas constant, being k_B the Boltzmann constant and N_A the Avogadro's number, x_i the molar faction of component *i*, m_i its chain length and g_{LJ} is the radial distribution function of a LJ mixture of spheres at contact length σ. The g_{LJ} function fitted to simulation data provided by Johnson et al. (1993) was used. The expression defining this pair correlation function is defined as:

$$g_{LJ}(\sigma)=1+\sum_{p=1}^{5}\sum_{q=1}^{5}a_{pq}\left(\rho_c\right)T^{1-q} \tag{III.1.8}$$

where a_{pq} are the constants fitted to simulation data, ρ_c is the density of Lennard Jones cores and *T* is the temperature. Note that this contribution is readily applicable to mixtures. At this point it is convenient to stress that the first order of the theory developed by Wertheim (TPT1) presents several limitations. At this level the formation of ring like structures, when associating, was neglected, and only tree like structures are considered, the second limitation is that each associating site is only allowed to form one single bond, and finally, all sites of the molecule are equivalent and independent of each other. The

consequence of this is that the theory neglects any steric effects that might possibly exists due to the extreme proximity of two repulsive sites.

The association term, A^{assoc}, is added when the fluid under study has an associating behavior (i.e. possible formation of hydrogen bonds). The association Helmholtz free energy depends mainly on X^{α}, the fraction of molecules not bonded at site α. The computation is performed over all association sites on the molecule and for all associating species present in the mixture.

$$A^{assoc} = RT \sum_i x_i \left(\sum_{\alpha} \ln X_i^{\alpha} - X_i^{\alpha} + \frac{M_i}{2} \right) \tag{III.1.9}$$

where M_i is the number of association sites per molecule, and α is the running label for the association sites, which are labeled with capital roman letters, and the sum extends over all i compounds in the mixture. The specific expression for X^{α} is given by:

$$X_i^{\alpha} = \frac{1}{1 + \rho \sum_j x_j \sum_{\beta} X_j^{\beta} \Delta^{\alpha_i \beta_j}} \tag{III.1.10}$$

It relates the number of bonded molecules (or non-bonded molecules) to two molecular parameters, ε_{HB} and $k_{HB,}$ the energy of the association site and the volume of association, respectively, through the association strength, $\Delta^{\alpha_i \beta_j}$, which denotes the association strength between site α on molecule i and site β of molecule j. The general expression for the association strength is given by:

$$\Delta^{\alpha_i \beta_j} = \int g_R^{ij}(12) e^{\frac{\varepsilon_{HB}^{\alpha_i \beta_j}}{k_B T}} d12 \tag{III.1.11}$$

where g_R is the pair correlation function.

In the context of the soft-SAFT EoS the association interactions are modeled as being embedded in the Lennard Jones core and tangent to the surface. This approach can be used when a soft reference fluid such as the Lennard Jones ones is used, which is the case of the soft-SAFT EoS. A scheme of the association geometry is shown in Figure III.1.2.

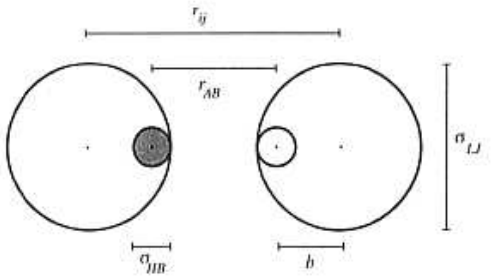

Figure III.1.2: Two dimension view of the geometrical configuration of the association sites in Lennard Jones spheres. Figure taken from literature (Müller and Gubbins, 1995)

The mathematical description of the described approach was developed by Walsh and Gubbins (1993) and Johnson and Gubbins (1992). The resulting expression for the associating strength is:

$$\Delta^{\alpha_i \beta_j} = 4\pi \left(e^{\frac{\varepsilon_{HB}}{T}} - 1 \right) k_{HB} I \tag{III.1.12}$$

where I is an integral which is defined as:

$$I = \frac{1}{24 b^2 \sigma^3} \int_{2b-\sigma_a}^{2b+\sigma_a} g_R(r) (\sigma_a + 2b - r)^2 (2\sigma_a - 2b + r) r \, dr \tag{III.1.13}$$

Fitting this equation to the simulation data of the Lennard Jones fluid, the integral becomes and solving it numerically it becomes:

$$I = \frac{1}{38400} \sum_{p=0}^{4} \sum_{q=0}^{4} a_{pq} \rho_c^{\,p} T^q \tag{III.1.14}$$

The number of association sites for each molecule, as well as the allowed interactions among the sites, has to be specified a priori within the SAFT approach. All association interactions are considered to be equivalent, i.e., all sites have the same values for the ε_{HB} and k_{HB} parameters.

A multipole term can also be added to model molecules where these properties are important and thus influence the thermophysical properties of the compound under study. The leading multipole term for fluids of linear symmetrical molecules, such as carbon dioxide, acetylene, etc., is the quadrupole-quadrupole potential (Gubbins and Twu, 1978), which introduces a new parameter, the quadrupole moment Q, for each compound able to show this type of electrostatic interactions. An expansion of the Helmholtz free energy in

terms of the perturbed quadrupole-quadrupole potential with the Padé approximation was proposed by Stell et al. (1974).

$$A^{qq} = A_2^{qq}\left(\frac{1}{1-\frac{A_3^{qq}}{A_2^{qq}}}\right) \qquad \text{(III.1.15)}$$

Expressions for A_2 and A_3, the second and third-order perturbation terms, were derived for an arbitrary intermolecular reference potential and can be found in the original papers (Gubbins and Twu, 1978; Stell et al., 1974; Twu et al., 1975 and Twu, 1976).

The main terms of the soft-SAFT used in the present work are listed above. Additional terms can be added to further improve the abilities of the equation, such as dipolar terms (Ghosh et al., 2003) or electrolyte terms (mean spherical approximation MSA (Li et al., 2000)) or even a density gradient theory (DGT) to study interfacial properties (Kahl and Enders, 2000, Duque, et al., 2004 and Mejia et al., 2005), making this model very modular and flexible.

The quadrupolar interactions present in systems with components such as carbon dioxide, benzene or nitrogen need also to be taken into account in a molecular modeling approach. These electrostatic interactions have been modeled with and without the inclusion of the quadrupolar term in SAFT type equations. Note that in the second case, the quadrupolar contribution is *effectively* included in the value of the other molecular parameters (Colina et al., 2004). Although this is a valid approach, since all parameters are effective, it does not allow the investigation of the explicit contribution that the quadrupole has to the global behavior of the mixture. In the case of explicit inclusion of quadrupolar interactions, which is the approach used in this work, a new parameter, Q, needs to be taken into account,. The formalism used to model this kind of interaction is the one proposed by Twu and Gubbins (1978). The quadrupolar moment is modeled as being effectively present in a fraction of the segments of the molecule (x_p), p. e., one third of the carbon dioxide molecule actually "carries" the quadrupole moment. The value of the molecular parameter Q is obtained in the usual way, by fitting to experimental data. However, care is taken so that the chosen value of Q is sound as compared to that found by experimental or *ab-initio* methods. The fraction x_p is chosen depending on the molecules'

geometry. With x_p and Q fixed, only the usual three molecular parameters need to be adjusted for the quadrupolar molecules (CO_2, benzene and nitrogen) as it happens for the non-quadrupolar molecules (hexane, propane and methane): m, the chain length and σ and ε, the size and energy parameters of the groups forming the chain. These three parameters are fitted in each case to experimental vapor-liquid equilibrium data for the pure compounds or taken from previous works.

III.1.1. Applying the SAFT EoS to polymers phase equilibria

The modeling of polymer phase equilibria with SAFT-type equations and related approaches poses two problems: the calculation of the polymers pure component molecular parameters, due to the lack of vapor pressure in polymer melts, and the numerical problems due to the large asymmetry of polymer-solvent/gas systems. Modeling the vapor-liquid equilibria of polymer solutions is a challenge also from the numerical point of view. In this type of phase equilibria, no polymer molecules are present in the gas phase, as it does not have a measurable vapor pressure, only the solvent is present.

For lower molecular weight substances, the EoS parameters are found by fitting the saturation density and vapor pressure data of the pure compound. For polymers this is not possible since they have no measurable saturation pressure. Also, the temperature range at which the density is measured is quite narrow, as they decompose at higher temperatures, still far away from the theoretical critical point of the large molecule (Pamiès and Vega, 2002). Thus, new methods have to be developed in order to enable the estimation of these parameters for heavy molecules, such as polymers, within the SAFT approach.

The fitting of SAFT parameters for polymers is a very debated problem (Gross and Sadowski, 2002 and Kouskoumvekaki, 2004a): the problem is that the parameters obtained by fitting only to the density data of pure polymers provide poor descriptions of the mixtures behavior, hence lacking transferability. One of the proposed solutions was to fit the polymer parameters to a polymer binary mixture (Gross and Sadowski, 2002). This is a

rather controversial procedure, as the fitted parameters may be suitable just for that system and may not be transferable to other related binaries with the same polymer, but with others solvents that have different characteristics, like for instance associating compounds. Another question that arises from this procedure is how much of the binary interaction parameter is incorporated into the polymer parameters, and vice-versa, how much of the polymer parameters is incorporated into the binary interaction parameter. A solution presented by Kouskoumvekaki et al. (2004a) consists in using only using the pure polymer pVT data. Using the *n*-alkane series the author assumes that for zero molecular weight all polymers become indistinguishable so the correlation of parameters of the polymers would give the same values for every polymer at a molecular weight of zero. With this assumption, the only values that need to be found for setting up a correlation of molecular parameters are the slopes of the lines defined by the correlation equations. For this the first member of the series (e.g. ethylbenzene for polystyrene, isobutane for polyisobutane) is used to calculate the number of segments (m) and energy parameter (ε). Finally the size parameter (σ) is fitted to pure polymer pVT data. According to the author, the results obtained when using this method are good for the majority of the systems but fail to describe systems where both Lower and Upper Critical Solution Temperatures are present.

The scope of this work is to develop a model based on the soft-SAFT EoS, proposed by Blas and Vega (1997), for the description of vapor-liquid and liquid-liquid equilibria of polymer-solvent systems. In addition, to provide a methodology in which systematic studies on polymer solutions can be made by the use of transferable molecular parameters with molecular-based EoS. The performance of the soft-SAFT equation is compared with the PC-SAFT EoS, since PC-SAFT has been widely used for polymeric systems. Both equations proceed from a thermodynamic perturbation theory in which different perturbation terms are added to the chosen reference term. The main difference between this two EoS's is the reference term. Both equations have proved to be accurate for phase equilibria calculations of several pure fluids and binary mixtures. While most of the applications of PC-SAFT deal with polymeric systems, the use of the soft-SAFT equation to long chain molecules has been very limited until the present study. In fact, regarding the calculation of thermodynamic properties of long chain molecules, soft-SAFT has been

applied, so far, to the calculation of critical points of homopolymer systems (Pamiès and Vega, 2002) and to study the solubility of hydrogen in heavy n-alkanes (Florusse et al., 2003), obtaining good agreement with available simulation and experimental data. Our objective here is to check the performance of this model for polymer solutions with different solvents.

Concerning polymer phase equilibria calculations, the components composition is usually presented as mass fractions, since the polymer has a much higher molecular weight than the solvent. The SAFT equation of state is defined in terms of molar fractions, which might present a problem when computing the solvent molar fraction as they might become very small leading to numerical problems. A similar problem may occur when modeling polymer vapor-liquid equilibria: in the gas phase there is virtually no polymer but thermodynamically this value cannot be zero, even tough it might be extremely low. This produces some difficulties in calculating phase equilibria via flash calculations. The asymmetry of the system leads to very low fugacities which may go past the underflow of the computer system. A solution to this problem was proposed by Ghosh and coworkers (2005), who assured the thermodynamics stability by using the tangent plane distance method. In the present work, the phase equilibria coexistence in equilibrium is assured by the equality of chemical potentials of each component in each phase, as well as the total pressure of each phase. Hence, the calculations presented here were performed using bubble pressure calculations and dew point calculations.

To use the existent piece of software to describe phase equilibria of polymer systems some modifications had to be made in the code, especially in the determination of phase coexistence equilibria due to numerical issues when using it with polymers. The phase equilibria is determined by the fugacity method (Fotouh and Shukla, 1996), which consists in imposing the equality of chemical potentials at fixed temperature and pressures. In the soft-SAFT case, as it is defined explicitly as a function of temperature, density and composition, the fugacity method is applied by additionally imposing the equality of pressures. When using this approach for polymer phase equilibria modeling, namely vapor-liquid equilibria, a problem usually arises from the fact that the composition of polymer in the vapor phase is zero (or very close to zero). This problem comes from the fact that the

chemical potential of the vapor phase would never change for small changes in the global system composition, since it would only account for the presence of the solvent, but the liquid phase chemical potential would change since its composition is of a finite, numerically accountable value. This leads to the fact that, when using the fugacity method, the equilibrium would never be reached. To overcome this limitation, a condition was programmed in the existent software, which for extremely low compositions of one component in one of the phases (polymer in the vapor phase), it would ignore the equality of chemical potentials and considered only the equality of pressure of the two phases. This method was used throughout this thesis.

III.2. Polyethylene modeling

III.2.1. Introduction

In the previous section the modeling of the ethyleneglycol oligomers solution thermodynamics with the soft-SAFT EoS, developed by Blas and Vega (1997), lead to the modeling of the thermodynamic behavior of several mixtures and of poly(ethylene glycol). The transferability of the molecular parameters of the soft-SAFT EoS provided that this could be accomplished easily just by using the correlation of parameters of the oligomeric compounds of poly(ethylene glycol). For the polyethylene (PE) polymer a similar approach can be made. The extrapolation of the correlation of molecular parameters for the *n*-alkanes series (Pamiès and Vega, 2001) for higher molecular weights could be used to model polyethylene polymers. This seams to be a very good approach since a polyethylene can be thought of as an extremely large *n*-alkane. In fact it is a very good approach for describing the pure polymer phase equilibria as it will be discussed in this chapter. On the other hand it perform badly when modeling the phase equilibria behavior of polymer mixtures, in particular the liquid-liquid phase equilibria.

In this work, the modeling of the vapor-liquid and liquid-liquid phase equilibria of polyethylene solutions with the soft-SAFT EoS will be addressed. Additionally a method to find the soft-SAFT EoS molecular parameters for the polyethylene polymer will be developed, improving the correlation of parameters of the *n*-alkanes. A side-by-side comparison with the PC-SAFT EoS, developed by Gross and Sadowski (2001) will also be made. This equation has already proven to successfully describe the phase equilibria of polymer solutions (Gross and Sadowski, 2002; Kouskoumvekaki et al., 2004a and 2004b; von Solms et al., 2003, 2004 and 2005). Both equations were developed from the same perturbation theory with the only difference lying in the reference term.

III.2.2. Pure polyethylene parameters

To adequately describe the phase behavior of a mixture with the soft-SAFT equation of state, the molecular parameters for the pure compounds need to be estimated first. Due to the absence of vapor pressure of polymer melts, two different approaches are used here.

First, polyethylene molecular parameters were obtained by extrapolation of the correlation of parameters with molecular weight from the *n*-alkane series (Pamiès and Vega, 2001):

$$m = 0.0255\,M_n + 0.628 \qquad \text{(III.2.1a)}$$

$$m\sigma^3 = 1.73\,M_n + 22.8 \qquad \text{(III.2.1b)}$$

$$m\varepsilon/k_B = 7.89\,M_n + 38.0 \qquad \text{(III.2.1c)}$$

where m is the length of the chain of segments, σ is the size of each segment (LJ diameter), ε is the energy of the segments and M_n is the number molecular weight (in g/mol). Units of σ and ε/k_B are in Å and K, respectively. We have derived a similar correlation for the PC-SAFT equation using the molecular parameters given by the authors (Gross and Sadowski, 2001), in a similar way as done by Pàmies and Vega (Pamiès and Vega, 2001):

$$m = 0.0257\,M_n + 0.844 \qquad \text{(III.2.2a)}$$

$$m\sigma^3 = 1.73\,M_n + 19.36 \qquad \text{(III.2.2b)}$$

$$m\varepsilon/k_B = 7.01\,M_n + 109.44 \qquad \text{(III.2.2c)}$$

The notation is the same as in Eq. III.2.1.

These correlations make possible the calculation of molecular parameters for polyethylene with different molecular weights.

Figure III.2.1 depicts the density behavior with respect to temperature of a linear polyethylene with Mn = 16000 calculated with the correlations of Eqns. III.2.1 and III.2.2 for the soft-SAFT and PC-SAFT EoS's, respectively. The results obtained are compared to those obtained by the Tait equation using parameters found in the literature (Danner and High. 1993). The prediction of the density dependence with temperature calculated with the soft-SAFT EoS using the extrapolation of the molecular parameters correlation for the

alkane series (Pamiès and Vega, 2001) agrees very well with the one predicted by the Tait equation. The Average Absolute Deviation (AAD) is of 0.14 %.

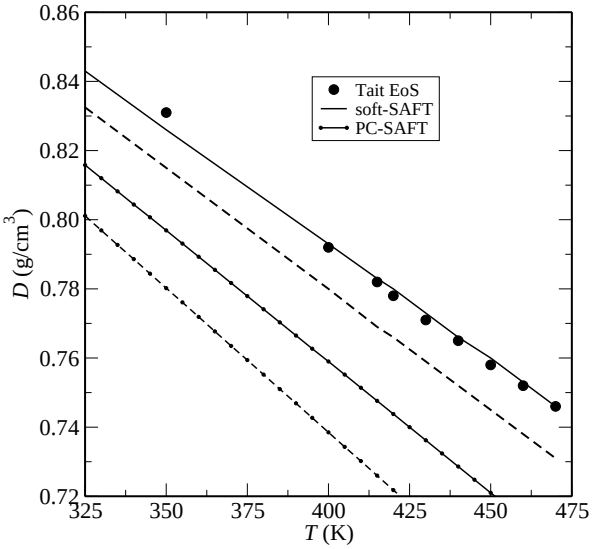

Figure III.2.1: Polymer melt density of a polyethylene with a Mn = 16000 at a pressure of 0.1 MPa. Dots are some values calculated with the Tait EoS (Danner and High, 1993). The full lines are calculated with both, soft-SAFT and PC-SAFT EoS models using correlation of parameters for the n-alkanes series (see Table III.2.1); the dashed lines are the calculated densities using correlation of parameters developed in this work for the soft-SAFT and the parameters from literature for PC-SAFT (Gross and Sadowski, 2002). Lines with small full circles correspond to PC-SAFT calculations.

Although results for the pure polymer density are excellent, the results obtained for mixtures were not as accurate, as it will be shown later. This has been previously observed when applying SAFT-type equations to polymer solutions (Gross and Sadowski, 2002 and Kouskoumvekaki et al., 2004a). The most common approach to solve this is problem is to fit the polymer parameters to a polymer mixture, and then to use the new parameters to model that polymer's mixture. We took a different approach in this work: instead of fitting to a mixture, a new correlation for the energy parameter was derived, while the expressions for the chain length (m) and segment size (σ) remained the same as in equation III.2.1. The resulting expression for the energy has the following form:

$$\varepsilon / k_B = \frac{294.9\, M_n - 779.38}{M_n + 10.6643} \qquad \text{(III.2.3)}$$

As in the original work of Pàmies and Vega (2001), this equation was obtained by fitting the values of energy and molecular weight of the alkane series from methane to

n-octane. Emphasis was put on accurately describing the heavier members of the series, instead of obtaining an excellent overall agreement for all members of the series. With this expression the limiting value of the energy term is lowered to a value of 294.9 K in comparison with the one given by Eq. (III.2.1c), which is 309.4 K. Although the difference between these two limiting values is not large, the fact that this parameter value is repeated *m* times for each polymer molecule produces great differences in the final results, as will be shown later. A main advantage of this approach versus fitting to a mixture is that they are pure component parameters which can be used to describe several polymer mixtures, without using any mixture information in the fitting procedure, in a predictive manner. The results for the pure polymer density obtained for linear polyethylene with Mn = 16000 with this new correlation are also displayed in Figure III.2.1. Interestingly, the prediction of the pure polymer density using Eq. (III.2.3), yields an AAD of 1.7 %, which is larger than the one obtained when Eq. (III.2.1c) is used. However, the accuracy of the equation for the description of polyethylene mixtures is better, as will be shown in the next section.

Predictions of the polymer densities using PC-SAFT are also presented in Figure III.2.1, for comparative purposes. In a similar way, two sets of molecular parameters were used for these calculations. The full line represents results obtained with parameters extrapolated from the correlation for the *n*-alkane series (Eq. (III.2.2)), while the dashed line represents results with the parameters of linear polyethylene which were fitted to the mixture of polyethylene with ethane by the authors (Gross and Sadowski, 2002). Note that this is not the approach we have taken with the soft-SAFT equation here. Results obtained with the PC-SAFT EoS and both sets of parameters are not as accurate as those obtained with the soft-SAFT EoS, showing AADs of 4.0 % and 8.0 %, respectively.

The molecular parameters of the pure compounds used in this work are listed in Tables III.2.1 (polymers) and III.2.2 (solvents), along with their respective sources.

Table III.2.1: Molecular parameters of the SAFT EoSs for the polyethylene polymers used in this work

M_n (g/mol)	Model	m	σ (Å)	ε/k_B (K)	reference
16000	soft-SAFT	408.6	4.077	294.7	Eq. III.2.12
16000	soft-SAFT	408.6	4.077	309.4	Eqs. III.2.1a, III.2.1b and III.2.3
16000	PC-SAFT	411.93	4.064	272.45	Eq. III.2.23
16000	PC-SAFT	420.8	4.0217	249.5	(Gross and Sadowski, 2002)
76000	soft-SAFT	1938.6	4.078	294.8	Eqs. III.2.1a, III.2.1b and III.2.3
108000	soft-SAFT	2754.6	4.078	294.9	Eqs. III.2.1a, III.2.1b and III.2.3
15000	soft-SAFT	383.1	4.078	294.6	Eqs. III.2.1a, III.2.1b and III.2.3
64000	soft-SAFT	1632.6	4.078	294.8	Eqs. III.2.1a, III.2.1b and III.2.3
13600	soft-SAFT	347.4	4.077	294.6	Eqs. III.2.1a, III.2.1b and III.2.3
20000	soft-SAFT	510.6	4.078	294.7	Eqs. III.2.1a, III.2.1b and III.2.3
31700	soft-SAFT	809.0	4.078	294.8	Eqs. III.2.1a, III.2.1b and III.2.3

Table III.2.2: Molecular parameters of the soft-SAFT EoS for the solvents used in PE systems

	m	σ (Å)	ε/k_B (K)	k_{HB} (Å^3)	ε_{HB}/k_B (K)	Reference
n-pentane	2.497	3.901	246.6	-	-	Pamiès and Vega, 2001
n-hexane	2.832	3.929	254.4	-	-	Pamiès and Vega, 2001
butyl-acetate	3.728	3.634	262.7	-	-	this work
1-pentanol	2.420	4.051	283.7	2250	3450	Pamiès and Vega, 2001
ethylene	1.431	3.599	187.8	-	-	this work

III.2.3. Results and Discussion

Polyethylene-solvent/gas phase behavior was chosen to evaluate the performance of the soft SAFT EoS in the description of both VLE/GLE and LLE for polymeric systems. One of the reasons for choosing this polymer was the existence of a correlation of parameters for the *n*-alkane series (Pamiès and Vega, 2001); as polyethylene can be considered as a very large alkane, it would be possible to extrapolate these correlations for higher molecular weight molecules. Also, a series of solvents were chosen in order to obtain a rich

phase behavior, from vapor-liquid to liquid-liquid equilibria, with the aim of extensively evaluating the performance of the soft-SAFT model for polymer solutions.

The performance of the chosen equation and was investigated for a wide range of phase diagrams. We have modeled different types of polyethylene mixtures, ranging from liquid-liquid mixtures to vapor-liquid equilibrium mixtures and gas solubility. The solvents studied include non associating compounds such as alkanes and alkenes, polar compounds such as esters and associating compounds as alcohols.

III.2.3.1. Polyethylene / n-pentane

Predictions for the liquid-liquid phase equilibria diagram for the system of polyethylene, Mn = 16000 g/mol and Mw/Mn = 1.16, with *n*-pentane at a pressure of 5 and 10 MPa (Kirna and Zhuang, 1992) calculated using both sets of soft-SAFT and PC-SAFT polymer parameters are presented in Figure III.2.2. Calculations were performed with the molecular parameters of the pure components, in a predictive manner, i.e no binary interaction parameters were used. The advantage of using the new correlation proposed in Eq. (III.2.3) is clearly depicted in Figure III.2.2, where a better description of the phase behavior of the mixture at two different pressures is observed. The results obtained with soft-SAFT are equivalent to those obtained using the PC-SAFT with molecular parameters for polyethylene proposed by Gross and Sadowski (2002), which were calculated by fitting them to a mixture of polyethylene and ethene. It is interesting to remark that despite the differences between the two SAFT EoS in predicting the density of the pure polymer (see Figure III.2.1), both equations behave in a very similar way when describing LLE for mixtures.

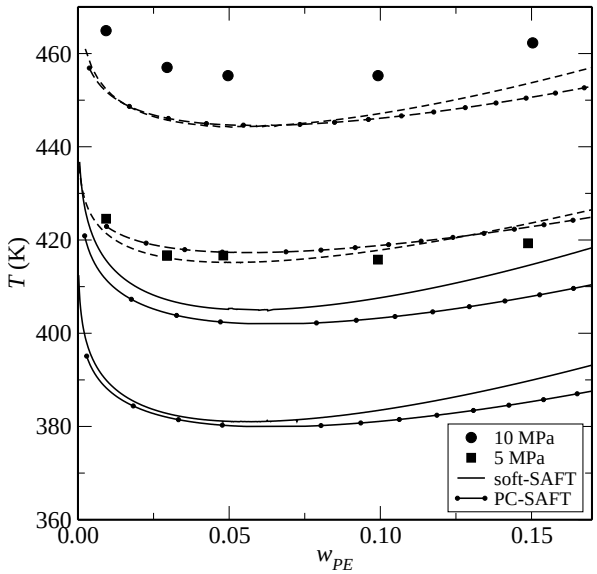

Figure III.2.2: Liquid-liquid equilibria of polyethylene (16000) and *n*-pentane using soft-SAFT and PC-SAFT. Line description as in Figure III.2.1. Experimental data from E. Kiran and W. Zhuang (1992).

Predictions of vapor-liquid equilibrium for a pentane - polyethylene (Mn= 76000g/mol) mixture (Surana et al., 1997) at two different temperatures are shown in Figure III.2.3. The polymer molecular parameters used in the soft-SAFT EoS were obtained from Eq. (III.2.3). For comparative purposes we also show the description of the PC-SAFT model. As in Figure III.2.2, no binary interaction parameters were used, results for the mixture were obtained from pure component parameters. The results obtained are in excellent agreement with the experimental data, indicating that both SAFT models provide a good description of both polymer vapor-liquid and liquid-liquid equilibrium using these parameters.

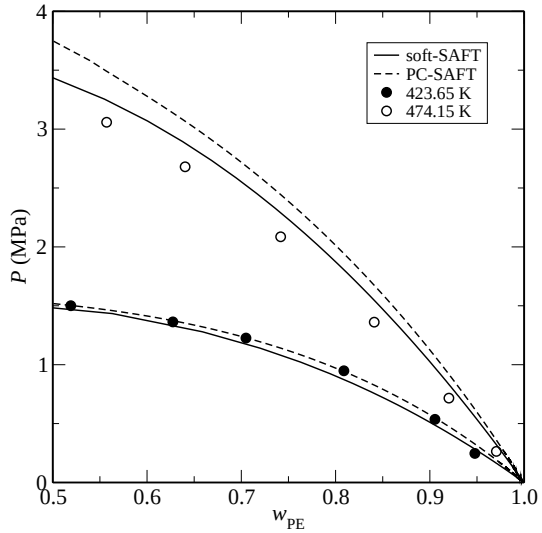

Figure III.2.3: Modeling of the isothermal vapor-liquid equilibria of polyethylene (Mn = 76000) and *n*-pentane with the soft-SAFT EoS (full lines) and with the PC-SAFT (dashed lines) EoS. Experimental data from Surana et. al. (1997).

III.2.3.2. Polyethylene / n-hexane.

Chen et al. (2004) measured the liquid-liquid equilibria of polyethylene and *n*-hexane. The polymer was bimodal with number molecular weights of 15000 and 108000 g/mol. We have modeled this bimodal polymer as a mixture of two polymers, which in this case is a polymer equimolar mixture. The two separated polymer binary systems, polyethylene (Mn=15000 g/mol)/*n*-hexane and polyethylene (Mn=108000 g/mol)/*n*-hexane, were also modeled and the results are shown in Figures III.2.4 and III.2.5, respectively. Again, the polymer molecular parameters were obtained from Eq. (III.2.3) and no binary interaction parameters were used. Note that for the heavier polymer the critical point of the mixture is well predicted but the subcritical region is underestimated, while for the lower molecular weight polymer the critical point is overestimated. The bimodal polymer modeling results are shown in Figure III.2.6 at 453.15 K. The phase equilibrium description for the bimodal mixture is well achieved by the soft-SAFT model, especially considering that this is a very challenging system and the curves correspond to pure predictions.

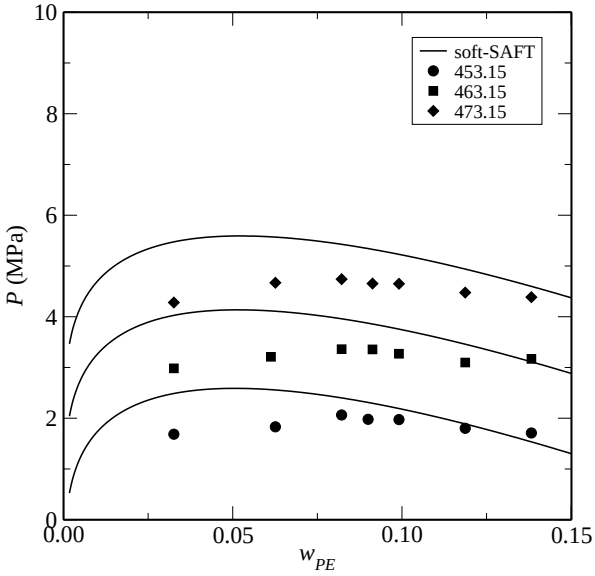

Figure III.2.4: Liquid-liquid equilibria of a mixture of polyethylene (Mn = 15000) and *n*-hexane at isothermal conditions. Line, soft-SAFT predictions. Symbols, experimental data taken from literature (Chen et al., 2004).

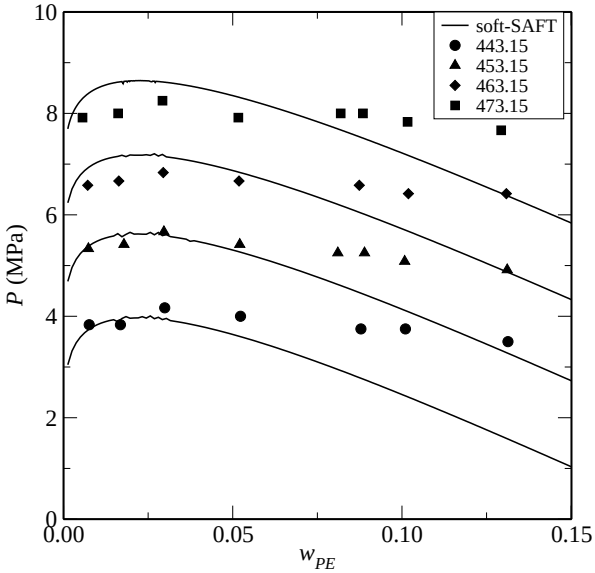

Figure III.2.5:Liquid-liquid equilibria of a mixture of polyethylene (Mn = 108000) and *n*-hexane at isothermal conditions. Line, soft-SAFT predictions. Symbols, experimental data taken from literature (Chen et al., 2004).

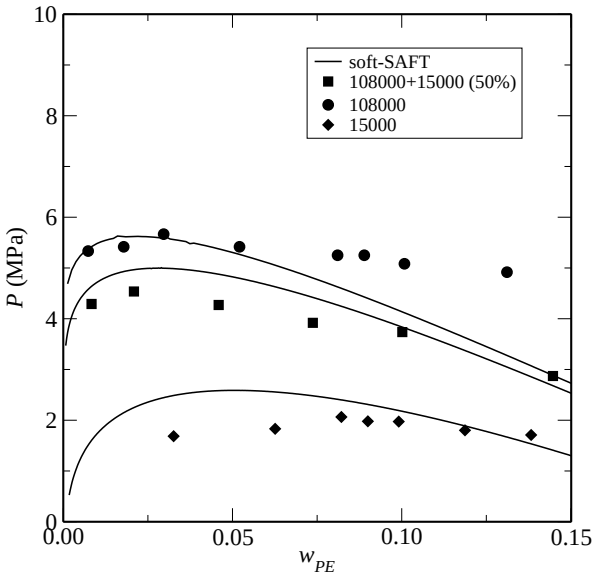

Figure III.2.6: Liquid-liquid equilibria of a mixture of a bimodal polyethylene (Mn_1 = 15000 and Mn_2 = 108000) and n-hexane at isothermal conditions. Comparison with the pure polyethylenes of molecular weights 15000 and 108000 is presented. Line, soft-SAFT predictions. Symbols, experimental data taken from literature (Chen et al., 2004).

III.2.3.3. Polyethylene / butyl acetate

Besides mixtures with just an UCST or a LCST, it is also of interest to describe systems with two (LCST and UCST) critical points. Figure III.2.7 shows the soft-SAFT description of the mixture of polyethylene (Mn=64000 and Mn=13600 g/mol) and butyl acetate where the experimental data was taken from Kuwahara et. al. (1974). This mixture shows an UCST and a LCST behavior, being a challenging mixture to any modeling approach.

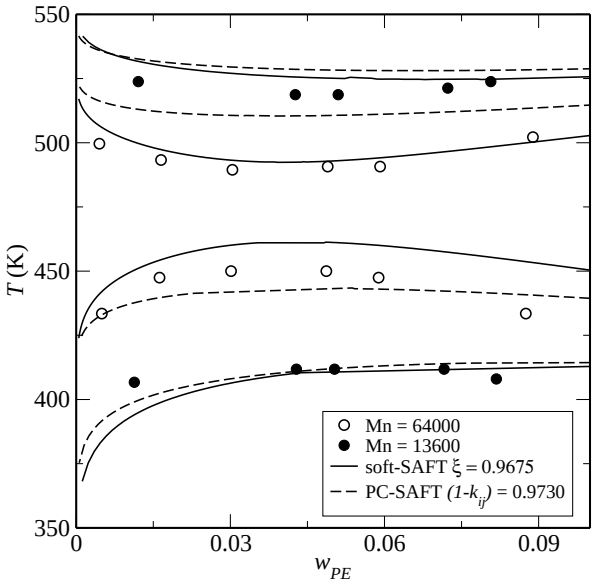

Figure III.2.7: Liquid-liquid phase equilibria modeled with the soft-SAFT EoS (full lines) and the PC-SAFT EoS (dashed lines) of a mixture of polyethylene and butyl acetate at a constant pressure of 0.1 MPa, with a fit binary parameter to literature data (symbols)(Kuwahara et al., 1974).

Calculations made with pure component parameters (as done in the previous cases) lead to an extremely low underprediction, giving a UCST of around 150K when the experimental value is around 420K for the lower molecular weight polymer. The use of one binary interaction parameter was needed to obtain a reasonable description of the low temperature region, although no influence of this parameter was observed for the high temperature region. This fact leads to the conclusion that the lower temperature phase coexistence diagram is driven by the energy of interaction of the molecules, since the binary parameter is a correction to this energy of interaction. Results obtained with PC-SAFT, also with a binary parameter present a similar behavior, although the predictions deteriorate near the LCST, which are slightly overestimated compared to soft-SAFT calculations. It is remarkable the description provided with both equations with just one binary parameter, and very close to unity ($\xi_{soft\text{-}SAFT} = 0.9675$; $\xi_{PC\text{-}SAFT} = (1\text{-}k_{ij}) = 0.9730$).

III.2.3.4. Polyethylene / 1-pentanol

The use of associating solvents adds extra complexity to the system. To check the accuracy of the equation we have investigated the description of a mixture of polyethylene

(Mn = 20000g/mol) with pentanol (Nakajima et al., 1966) using the soft-SAFT EoS. The results obtained with the parameters provided in Tables III.2.1 and III.2.2 are shown in Figure III.2.8. A binary interaction parameter with a value of 0.9873 was needed, as otherwise the phase coexistence would be underestimated. The data available is rather scarce, making difficult to assess the accuracy of the soft-SAFT EoS.

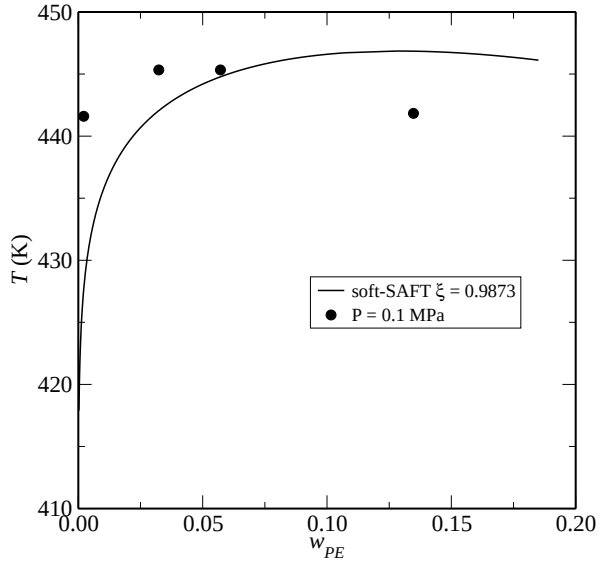

Figure III.2.8: Phase behavior description of the soft-SAFT EoS of a polyethylene with a number molecular weight of 20000 mixed with *1*-pentanol. A binary interaction parameter was fit to experimental data reported in literature(Nakajima et al., 1966). Lines, soft-SAFT EoS; symbols, experimental data.

III.2.3.5. Polyethylene / ethylene

The description of the phase equilibria of the polymer with its monomer is of the utmost importance, as they coexist throughout the whole manufacturing process. It starts in the reaction itself, but the most important step is the separation of unreacted monomer from the polymer. This is usually done in flash vessels specifically made for this purpose. In order to predict the flash operation, accurate phase equilibria data is needed. We have also described the gas-polymer phase equilibria with the soft-SAFT EoS. The results are depicted in Figure III.2.9, where the solubility of ethylene in polyethylene (Mn = 31700) (Hao et al., 1992) is represented.

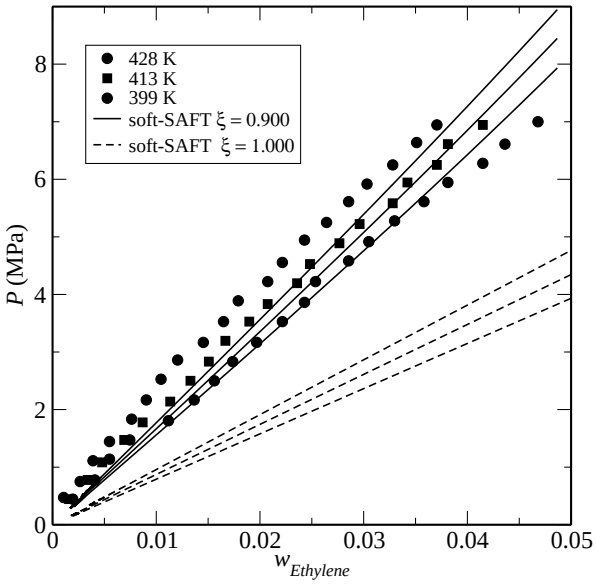

Figure III.2.9: Gas solubility of ethylene in polyethylene (Mn = 31700). Full lines represent the soft-SAFT model with an adjusted binary interaction parameter and dotted lines are the calculations of the mentioned model without binary interaction parameters. The experimental data was extracted from the literature (Hao et al., 1992).

It is observed that pure component parameters clearly underestimate the pressures, while a binary interaction parameter (0.900) provides good estimations of the vapor pressure of the mixtures. Even with the use of this binary parameter the mixture behavior is not exactly described by the soft-SAFT EoS, the equation is not able to capture the shape of the solubility curves. An explanation is the fact that the soft-SAFT EoS does not consider the possible degree of crystallization present in the polymer. This is particularly important in gas-polymer equilibria as the polymer is not being dissolved, but instead, it is the gas that is dissolving into the polymer. In pure polyethylene, the fraction of polymer that is in crystal form can reach 100% if the polymer is linear. At the modeled conditions, that is, high concentration of polymer, it is possible that some of the polymer exists in the crystal form. This is not taken into account explicitly in the soft-SAFT (and PC-SAFT) EoS.

III.2.4. Conclusions

We have shown here the accuracy of the soft-SAFT EoS to model the phase equilibria of polyethylene with several solvents, including pentane, hexane, butyl acetate, pentanol and ethylene. Results obtained with soft-SAFT were compared with experimental data and with the performance of the PC-SAFT EoS for the same systems.

We have circumvented one of the main drawbacks of using EoSs to model polymer systems, namely the difficulty to obtain the pure polymer parameters. This has been done with two alternative ways: (1) by using the molecular parameters obtained for the n-alkane series to model polyethylene, and (2) by proposing a new correlation of the energy parameter with the molecular weight, while keeping the size and chain length parameters from the correlation of the n-alkane series. The new correlation is able to accurately describe the behavior of polymer mixtures with various solvents, in better agreement with experimental data than the original n-alkanes correlation.

The accuracy of the soft-SAFT EoS for these polymeric systems has been proved in several ways: the equation was able to capture the vapor-liquid dependence with temperature, the simultaneous existence of upper critical solution temperature and lower critical solution temperature for the mixture with butyl acetate, and the gas solubility in polyethylene. The polymer/n-alkane systems were predicted from pure component parameters, while one energy binary parameter, close to unity, was needed in order to describe the polymer with butyl acetate, 1-pentanol and ethylene binary mixtures. The comparison between results obtained with soft-SAFT and PC-SAFT shows that both equations provide similar results in most of the cases, being soft-SAFT slightly more accurate for some particular mixtures.

III.3. Polystyrene

III.3.1. Introduction

In the previous chapter, the performance of the soft-SAFT EoS for describing polyethylene vapor-liquid and liquid-liquid phase equilibria was explored. Besides the study of the phase behavior of polyethylene mixtures, the work also dealt with different approaches to obtain the molecular parameters of the pure polymers, still an open question when using equations of state based models for polymer phase equilibria calculations. For poly(ethylene) systems an improved correlation for the energy parameter obtained by fitting the values of energy as a function of molecular weight for the alkane series from methane to octane only. The size and chain length parameters from the original Pàmies-Vega (2001) correlation were kept. A main advantage of this approach versus fitting to a mixture is that these parameters are pure component parameters, which can be used to describe several mixtures, without using any mixture information, in a predictive manner. The main limitation of the previous approach for polystyrene (PS) mixtures, such as the ones presented in this work, is the absence of a correlation for the light members of the series. Hence, alternative approaches to obtain the molecular parameters for pure polymers had to be explored. Recently, Kouskoumvekaki and coworkers (Kouskoumvekaki et al., 2004a) proposed a new method to estimate the molecular parameters for pure polymers. In this method, the molecular parameters of the polymer are found by correlating the number of segments (m) and the energy parameter (ε), using the repeating unit of the polymer under study, which is ethylbenzene in the case of polystyrene. The parameters correlation is similar to the one usually used for *n*-alkanes and assumes that in the limit of zero molecular weight all polymers are similar, i.e. the interception values of the correlation equations are considered to be the same for all polymers. The remaining parameter, the size parameter, σ, is then fitted to pure polymer pVT data in a wide range of temperatures and pressures. Despite the attractiveness of this method, which only uses information from the

polymer and its repeating unit, it did not provide sound results when describing the liquid-liquid phase equilibria of polystyrene (Kouskoumvekaki et al., 2004a). It will be shown here that this is especially true for liquid-liquid equilibria of polystyrene mixtures with a Lower and an Upper Critical Solution Temperature (LCST and UCST), where the model shows difficulties in describing both critical points.

Therefore, in order to find the polymer's molecular parameters for both soft-SAFT and PC-SAFT EoSs, we have decided to follow the approach followed by Gross and Sadowski (2002), which consists in fitting the pure polymer parameters to a binary mixture, and compare its performance with the method developed by Kouskoumvekaki et al (2004a).

To model the phase equilibria of polystyrene systems, a different reference EoS with soft-SAFT. The Kolafa and Nezbeda (1994) approach was used to describe the reference fluid term, while Blas and Vega used the modified Benedict-Webb-Rubin EoS derived by Johnson et. al. (1993) for the same purpose. The Kolafa and Nezbeda equation consists of a hard-sphere term with a dispersion term, both accounting for the Lennard-Jones reference contribution, and it was already used within the soft-SAFT context by Pàmies and Vega (2002). The two models perform very similarly for the range for which both of them can be applied. However, while the Johnson et al. term performs better for the vapor phase and close to the critical point of pure compounds (Johnson et al., 1993), the Kolafa and Nezbeda model extrapolates better to the lower temperature regions.

III.3.2. Pure Polystyrene Parameters

As already discussed, the estimation of polymer's molecular parameters is a very delicate task and the success of the modeling of the polymer systems phase equilibria is strongly dependent on the quality of these parameters. Unfortunately, the use of correlations for energy, size and chain length parameters can not be used for polystyrene, since there is not a series of low molecular weight compounds which could be used to extrapolate and, hence, the correlation of parameters would not be meaningful using only ethylbenzene.

Alternatively, two other methods of calculating the polymer parameters are used: the method proposed by Kouskoumvekaki and coworkers (2004a), which uses solely the properties of the pure polymer, namely density in a wide range of temperatures and pressures, and is referred throughout this work as method I, and the approach adopted by Gross and Sadowski (2002), in which the molecular parameters of the polymer are fitted, along with the binary interaction parameter, to mixture experimental data, and will be referred as method II. The first method is thoroughly explained in the authors' work (and roughly in Chapter III.1.1) and it has the main advantage of making the model predictive in terms of description of the mixture phase equilibria. The main drawback lies in the modeling of systems with a complex phase behavior, such as solutions of polystyrene which have a LCST and a UCST, since even the simplified PC-SAFT EoS used is not able to produce an adequate representation of the experimental data (von Solms, 2003). The major drawback of the method proposed by Gross and Sadowski (2002), method II, is that it requires a set of binary experimental data to fit the polymer parameters; in this case, it is not clear how much of the mixture data is taken by the pure component polymer parameters.

The system used to estimate the polystyrene's molecular parameters was PS(405000 g/mol)/methylcyclohexane (Sanders and De Loos, 1997), which was the same used by Gross and Sadowski (2002) in PC-SAFT approach. The parameters found for the polystyrene polymer using both methods I and II are reported in Table III.3.1. The molecular parameters of the monomer (styrene) and of the repeating unit (ethylbenzene) are also shown for reference and comparison.

Table III.3.1: Molecular parameters of the soft-SAFT EoS for polystyrene using methods I and method II.

Polymer (method)	m/Mn	σ (Å)	ε/k_B (K)	Reference of exp data
Polystyrene (I)	0.0222	4.009	365.4	(Sanders and De Loos, 1997)
Polystyrene (II)	0.0167	4.120	303.0	(Sanders and De Loos, 1997)
Polystyrene (II) (Fig. III.3.11)	0.0271	3.960	329.0	(Imre and van Hook, 1997)

Figure III.3.1 depicts the performance of both methods of pure polymer parameter´s estimation for the soft-SAFT and PC-SAFT models. The molecular parameters of the different solvents used are provided in Table III.3.2. The deviations in the pure polymer parameters between both methods can be clearly observed when polystyrene mixtures are modeled. Thus, the method II is preferred and is going to be used in this chapter.

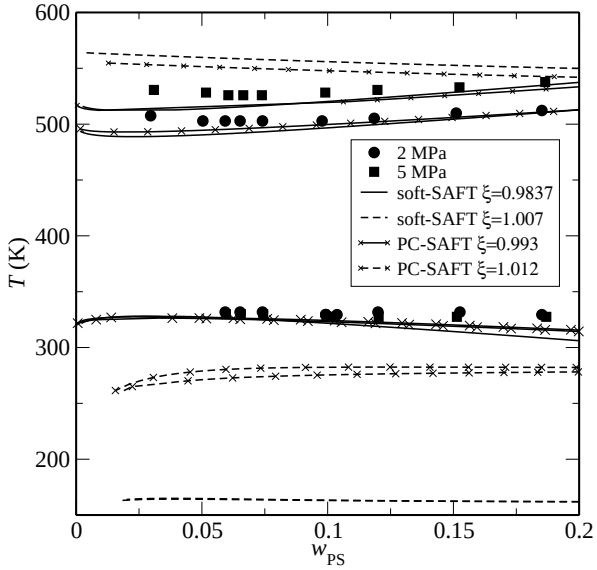

Figure III.3.1: Liquid-liquid of Polystyrene (Mn = 405000 g/mol) and methylcyclohexane. Experimental data points from literature (Enders and De Loos, 1997). Model description of the soft-SAFT and PC-SAFT model are shown using two methods for polymer's parameter calculation. Full lines: fitted to experimental data (method II), dashed lines: method of Kounskoumvekaki et. al (2004a) (method I).

Table III.3.2: Molecular parameters of the soft-SAFT EoS for the solvent used in PS systems.

Compound	m	σ (Å)	ε/k_B (K)	Q (C m^2)	ε_{HB}/k_B (K)	k_{HB} (Å)	ref.
Cyclohexane	2.362	3.971	294.92	-	-	-	DIPPR, 1998
Ethylbenzene	2.989	3.860	301.31	-	-	-	DIPPR, 1998
Ethylformate	2.811	3.354	255.24	-	-	-	DIPPR, 1998
Isopropyl Acetate	3.389	3.573	249.68	-	-	-	DIPPR, 1998
Methylcyclohexane	2.504	4.141	296.55	-	-	-	DIPPR, 1998
***n*-nonane**	3.831	3.990	269.16	-	-	-	DIPPR, 1998
Styrene	2.818	3.881	320.32	-	-	-	DIPPR, 1998
Carbon Dioxide	1.571	3.184	160.19	4.4×10^{-40}	-	-	Pedrosa et al., 2005
Benzene	2.048	3.970	306.1	9.8×10^{-40}	-	-	Pedrosa et al., 2005
Water	1.000	3.190	408.54	-	2367	2707	Blas, 1998
Toluene	2.374	4.013	305.2	9.8×10^{-40}	-	-	DIPPR, 1998

III.3.3. Results and Discussion

III.3.3.1. Vapor-liquid Equilibria

The first challenge proposed is the modeling of vapor-liquid equilibria, since the parameters were fitted to a liquid-liquid equilibria experimental data set. Figures III.3.2, III.3.3, III.3.4 and III.3.5 show the performance of the soft-SAFT EoS in describing the vapor-liquid equilibria of polystyrene systems with three different solvents: benzene, ethylbenzene, n-nonane and water.

The vapor-liquid equilibria of the system polystyrene/benzene (Danner and High, 1993), with the polymer's molecular weight ranging from 20000 g/mol to 900000 g/mol, is depicted in Figure III.3.2. The molecular parameters for the benzene were evaluated in

Chapter III.4. The description of the phase equilibria is accomplished with the soft-SAFT EoS without requiring the use of a binary interaction parameter, in a pure predictive manner. The phase equilibria diagram is represented in terms of solvent activity as a function of composition, as the representation in terms of temperature would not provide a careful analysis of the model description of the lower temperature data. The soft-SAFT EoS is able to accurately describe the vapor-liquid diagram over a wide range of temperatures, from 288.15 K up to 448.15 K, and polymer's molecular weight, correctly predicting the absence of influence of the polymer's molecular weight in the activity of the mixture.

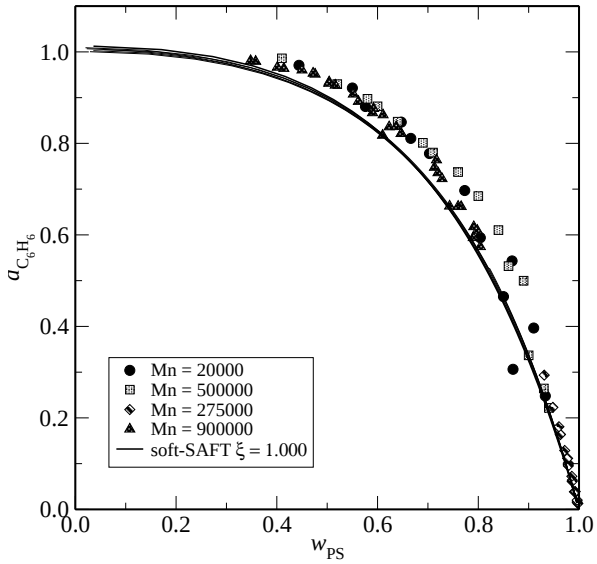

Figure III.3.2: Vapor-liquid equilibria of Polystyrene and benzene modeled with the soft-SAFT EoS. Experimental data taken from DIPPR handbook polymer solution thermodynamics (Danner and High, 1993).

Similar results are obtained for the system polystyrene/ethylbenzene (Sadowski et al., 1997) depicted in Figure III.3.3. The soft-SAFT calculations were, again, performed without using any binary interaction parameter. The results are now plotted as pressure versus composition in order to show how the soft-SAFT EoS describes the change in the total pressure of the system as a function of temperature. The results obtained using PC-SAFT EoS are also shown for comparison and they slightly underestimate the saturation

pressure of the mixture, which is not the case of soft-SAFT that provides an excellent representation of this system.

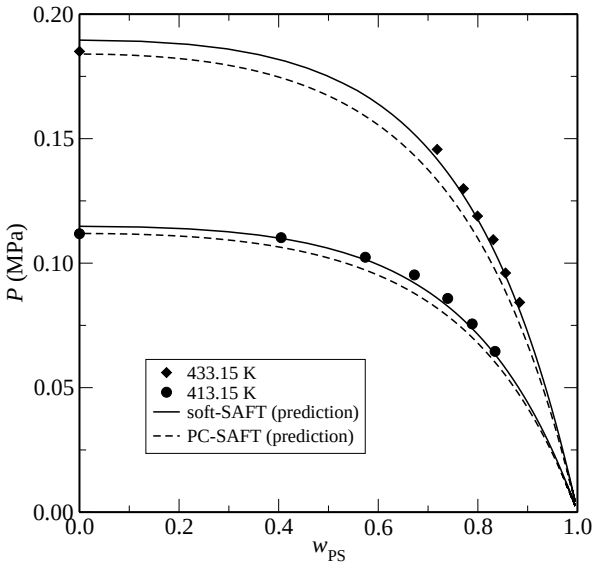

Figure III.3.3: Vapor-liquid equilibria of PS (Mn= 93000 g/mol) / ethylbenzene modeled with soft-SAFT and PC-SAFT EoS's. Experimental data from literature (Sadowski et al., 1997).

For the system polystyrene/n-nonane (Danner and High, 1993), presented in Figure III.3.4, the model behaves differently. Here, the soft-SAFT EoS tends to underestimate the saturation pressure, even when a binary interaction parameter is used. This behavior has already been observed in several other systems when the solvent deviates from being a spherical molecule (see, for instance, reference (Florusse et al., 2003)).

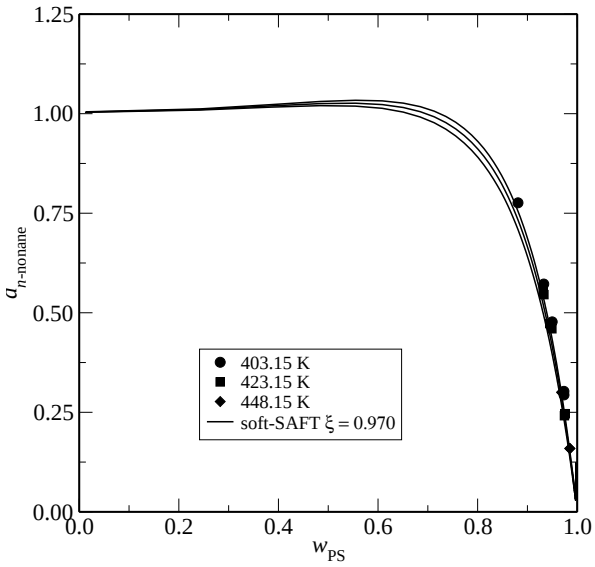

Figure III.3.4: Vapor-liquid equilibria of Polystyrene and *n*-nonane described using soft-SAFT. Experimental data taken from DIPPR handbook polymer solution thermodynamics (Danner and High, 1993).

An interesting system to study is the mixture PS / water and its phase equilibria. As water is an associating solvent, this system provides a way to access the quality of the polymer parameters as they were found using a mixture with a non-associating solvent (methylcyclohexane). A set of VLE data for the PS/water mixture was found in literature from Garcia-Fierro and Aleman (1985). Four isotherms between 297 and 345 K at 0.1 MPa were modeled. The phase equilibria description of this system with the soft-SAFT EoS is depicted in Figure III.3.5. The association model used for water considers four associating sites: two on the two hydrogen atoms and two on the oxygen atom. This model was proposed by Huang and Radsoz (1990) and has already been successfully used (Kraska and Gubbins, 1996a and 1996b). Although other models have been proposed for water, namely a three site model in which the oxygen atom is only allowed to form one bond (Huang and Radoz, 1990), this one was used here since this mimics the water molecule in a more realistic way. The agreement between the soft-SAFT and the experimental data is excellent when a temperature dependent interaction parameter is used.

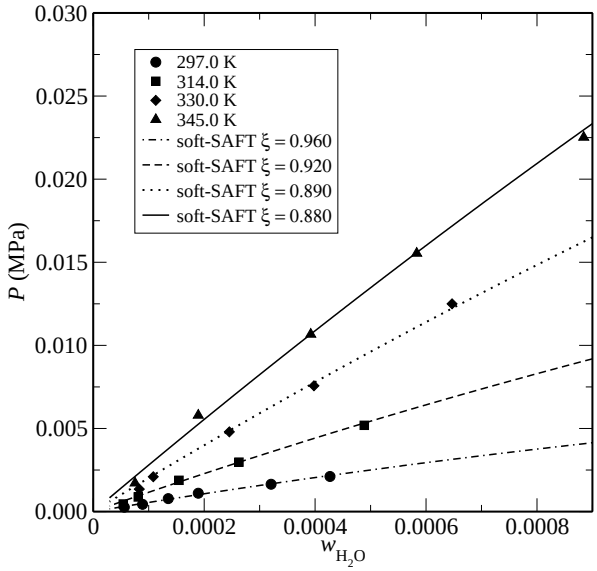

Figure III.3.5: Vapor-liquid equilibria of the system PS (68200 g/mol) / water modeled with the soft-SAFT EoS. Experimental data from Garcia-Fierro and Aleman (1985)

To assess the relative performance of the soft-SAFT equation of state against the studied GE models in Chapter II, a comparison, in terms of average deviations, between the soft-SAFT EoS and the GE models for the polystyrene / toluene mixture is presented Table III.3.3. It has to be taken into account that the results of the soft-SAFT EoS are predictions, that is ξ_{ij}=1.000, and they are superior to the results obtained with UNIFAC-FV. Also, the results obtained soft-SAFT are similar, for some systems, to the ones produced by the GE correlative models.

Table III.3.3: Average absolute deviation (%) obtained for the PS / toluene system (Tait and Abushihada, 1977; Baughan, 1948; Saeki et al., 1981; Scholte, 1970a; Scholte, 1970b; Bawn et al., 1950 and Cornelissen et al., 1963) with GE models ans soft-SAFT. The interaction parameters for the GE models presented were fitted to the data on the top row.

Mn_{PS}	NRF	Wu-NRTL	sUNIQUAC	UNIFAC-FV	soft-SAFT
10300	0.542	0.872	0.533	11.131	4.62
7500	0.680	1.253	0.611	6.299	3.49
49000	0.067	0.169	0.055	0.379	0.22
154000	1.889	1.738	1.930	2.397	1.04
200000	2.146	2.774	2.061	11.178	5.19
290000	1.431	1.823	1.354	8.497	3.78
435000	0.025	0.046	0.022	0.084	0.52
600000	5.306	5.108	5.349	6.932	2.78
a_{12}	-0.158	1.635	0.653	-	-
a_{21}	-0.022	-0.782	-0.323	-	-

III.3.3.2. Liquid-Liquid Equilibria

The soft-SAFT model description of the phase equilibria of a mixture polystyrene/cyclohexane is shown in Figure III.3.6. The experimental data was obtained from the DIPPR Handbook of Polymer Solution Thermodynamics (Danner and High, 1933) and from Choi et. al (1999).

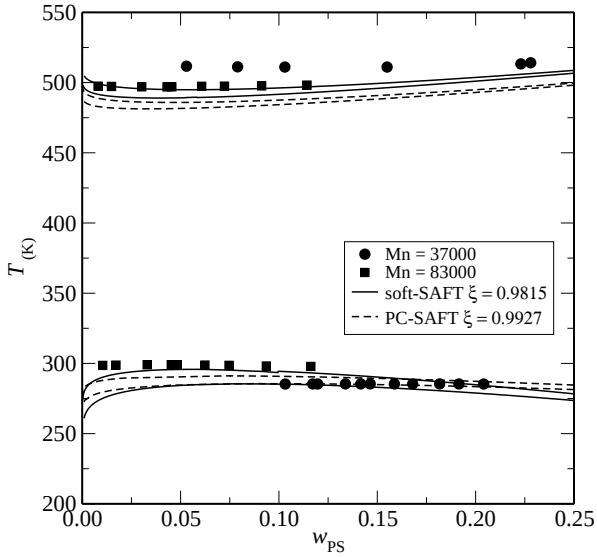

Figure III.3.6: Liquid-liquid equilibria of PS and cyclohexane at 0.1MPa. Experimental data from Danner and High (1933) for the polymer of Mn = 37000 g/mol and from Choi et al (1999) for the polymer with Mn = 83000 g/mol.

The molecular parameters for cyclohexane were estimated by fitting the saturation density and the vapor pressure of the pure compound experimental data (DIPPR, 1998) and are given in Table III.3.2. Two polymer molecular weights were considered: 37000 g/mol and 83000 g/mol, which are very different from the one to which the parameters were fitted. Despite this difference in the polymer's molecular weights, the soft-SAFT is able to scale them down to give a correct description of the liquid-liquid equilibria, namely the existence of both LCST and UCST. The same performance is verified for a mixture of polystyrene / methylcyclohexane, presented in Figure III.3.7a. It can be seen that the soft-

SAFT EoS can adequately describe the system UCST and its tendency with the molecular weight, especially for low molecular weight polystyrenes. The existence of a LCST for this system, as shown in Figure III.3.1, can also be predicted by both soft-SAFT and PC-SAFT EoS's. The results, depicted in Figure III.3.7b, show that the predicted LCST is very close in temperature to the one presented in Figure III.3.1, leading to the conclusion that it is not significantly dependent on the polymer's molecular weight.

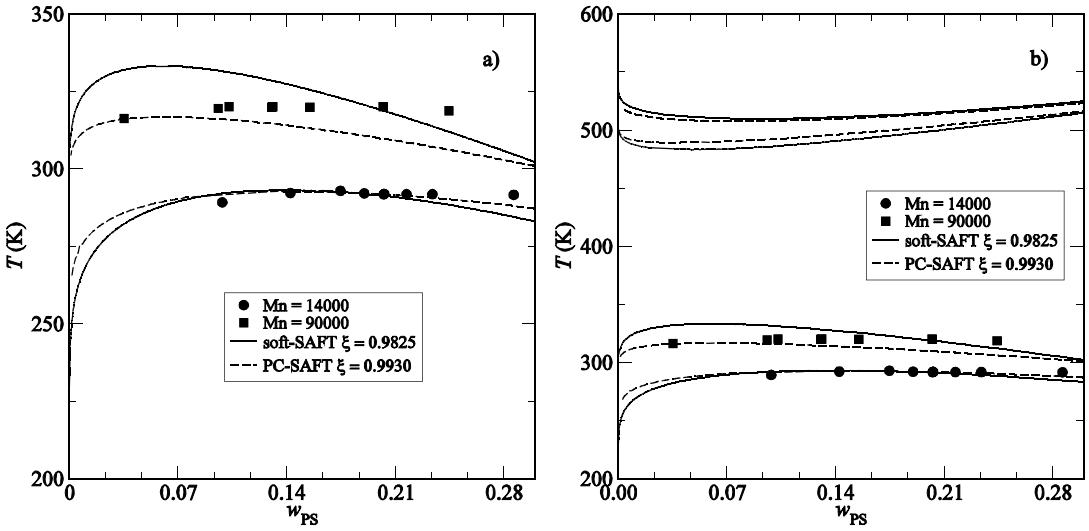

Figure III.3.7: (a) Liquid-liquid equilibria of PS, Mn = 14000 g/mol and 90000 g/mol, with methylcyclohexane modeled with PC-SAFT and soft-SAFT EoS. Experimental data was taken from literature (Wilczura-Wachnik and Hook, 2004). (b) Liquid-liquid equilibria of PS, Mn = 14000 g/mol and 90000 g/mol, with methylcyclohexane modeled with PC-SAFT and soft-SAFT EoS. Experimental data was taken from literature (Wilczura-Wachnik and Hook, 2004). Prediction of the existence of the LCST is shown for both soft-SAFT and PC-SAFT.

The liquid-liquid phase equilibria of benzene with polystyrene, with molecular weights ranging from 37000 g/mol to 2700000 g/mol, as modeled with both soft-SAFT and PC-SAFT, is presented in Figure III.3.8a. Despite the wide range of molecular weights, both models correctly describe the evolution of the phase equilibria with the molecular weight, but underestimating the value of the LCST. The existence of a LCST normally implies the existence of a UCST, as they behave like mirror images of each other, for very narrow molecular weight distributions. In fact, the existence of the UCST is the more common situation when a mixture has liquid phase split at low temperatures (Freeman and Rowlinson, 1960). However, sometimes the measurement of the UCST is not feasible as it

happens when the UCST is near the freezing point of the solvent, making operations like stirring, necessary to get a homogeneous distribution of particles at the phase split point, extremely difficult. According to the authors of the experimental data represented in Figure III.3.8a (Saeki et al., 1973), this was the cause that prevented the measurement of the UCST for this system. The SAFT approach can thus be a very useful tool in this sense, since it can be used to predict the UCST, as reported in Figure III.3.8b. The PC-SAFT EoS predicts the existence of the UCST around 270K, very near to the normal temperature of melting for benzene (278K), and the soft-SAFT predicts the UCST around 140 K, well bellow that value. For both models, the predicted temperature is, as expected, lower than the melting temperature for the pure solvent due to the freezing point depression. However, in this case, the PC-SAFT predictions are sounder considering the predicted temperature and the slight change of the UCST with the molecular weight of the polymer.

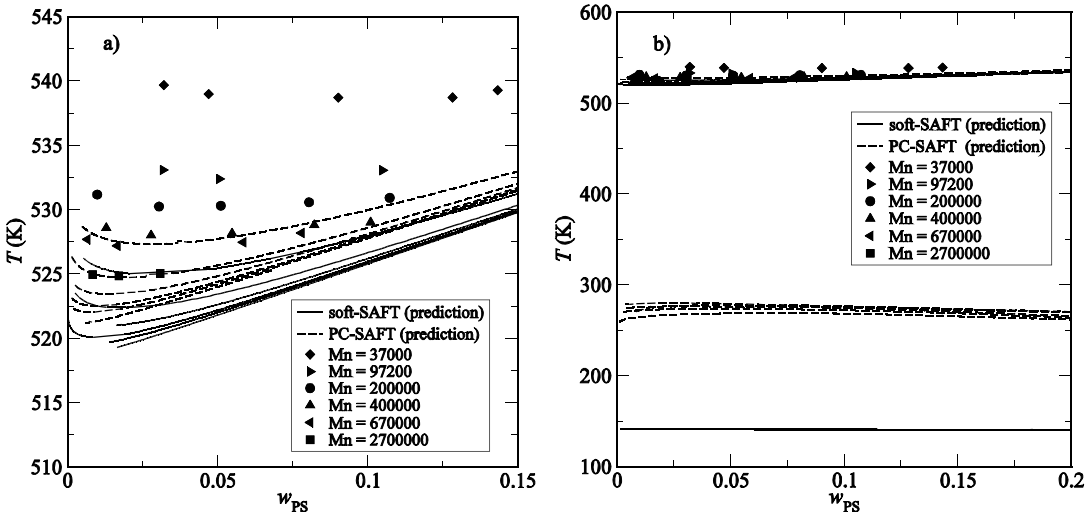

Figure III.3.8: (a) LCST modeling of the liquid-liquid equilibria of PS (several Mn) with benzene. Data taken from Saeki et al. (1973). (b) LCST modeling of the liquid-liquid equilibria of PS (several Mn) with benzene and prediction of the UCST. Data taken from Saeki et al. (1973).

The systems presented so far contained no polar molecules. In Figures III.3.9 and III.3.10, soft-SAFT and the PC-SAFT results for the liquid-liquid equilibria of polystyrene with two esters, ethyl formate and isopropyl acetate (Bogdanic, 2001), are shown.

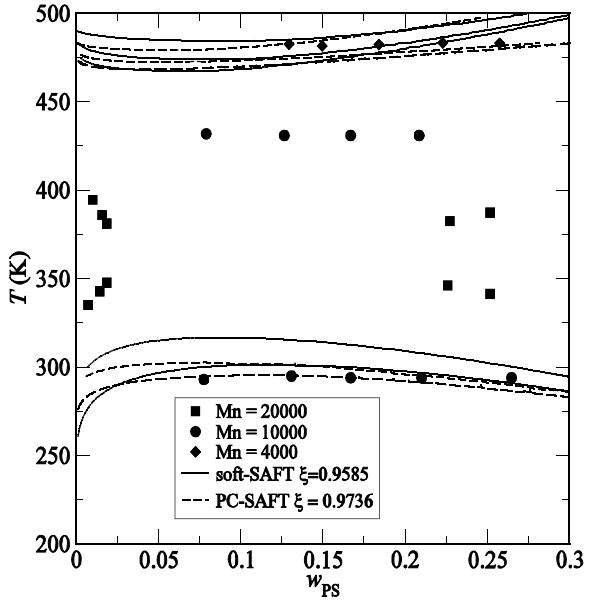

Figure III.3.9: Modeling of liquid-liquid equilibria of PS Mn = 4000 g/mol, 10000 g/mol, 20000 g/mol with ethyl formate. Data from Bogdanic et al (2001).

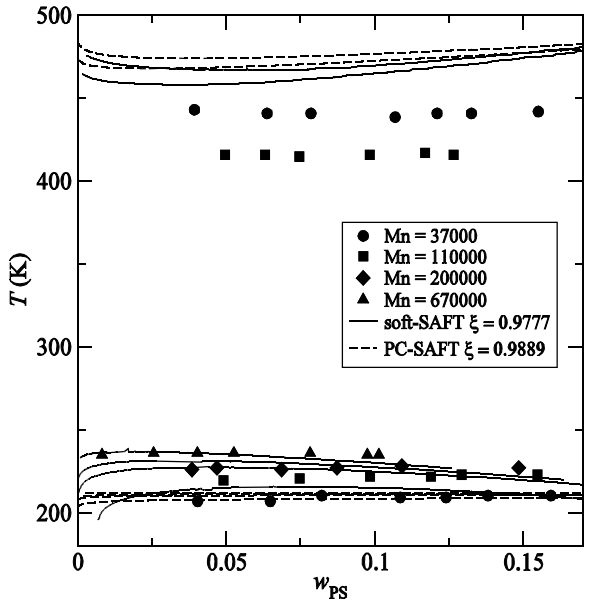

Figure III.3.10: Modeling of the liquid-liquid equilibria of PS, Mn = 37000 g/mol, 110000 g/mol, 200000 g/mol and 670000 g/mol, with isopropyl acetate using soft-SAFT and PC-SAFT. Data from Bogdanic et al (2001).

These two systems also present a LCST and an UCST. In the case of ethyl formate, the model cannot follow the tendency with the molecular weight of the polymer, nor to capture the hourglass type of phase diagram that this system presents for higher molecular weights,

even using a binary interaction parameter. The same limitation is observed for the PC-SAFT model. The liquid-liquid equilibria of polystyrene with isopropyl acetate was studied with polymer's molecular weights ranging from 37000 g/mol to 670000 g/mol. In this case, the soft-SAFT EoS successfully follows the tendency of the phase split with molecular weight only for the UCST. The LCST is overpredicted by the soft-SAFT EoS. We have performed the same calculations with the PC-SAFT EoS. As observed in the Figure, PC-SAFT also fails in the description of the UCST with the change of the polymer molecular weight, also overestimating the LCST.

So far, the polystyrene molecular parameters used enable a good description of liquid-liquid equilibria of polymer-solvent mixtures, despite some overpredictions of the LCST's. The description of LLE of the mixtures polystyrene/pentane, hexane and octane with a low molecular weight polymer (1241 g/mol) was also attempted but the obtained results are far off from the experimental data. This failure is due to the fact that the polystyrene parameters were calculated for a polymer with a molecular weight of 405000 g/mol. Thus, a new set of parameters for polystyrene was fitted to the mixture PS (1241 g/mol)/pentane and are then used for the other two solvents. With these new parameters, presented in Table III.3.1, the soft-SAFT EoS was able to correctly describe the mixtures PS/heptane and PS/octane, as it is shown in Figure III.3.11. Not surprisingly, the obtained parameters are closer to those for ethylbenzene than to the previously calculated parameters for PS 405000 g/mol, as can be compared in Table III.3.1.

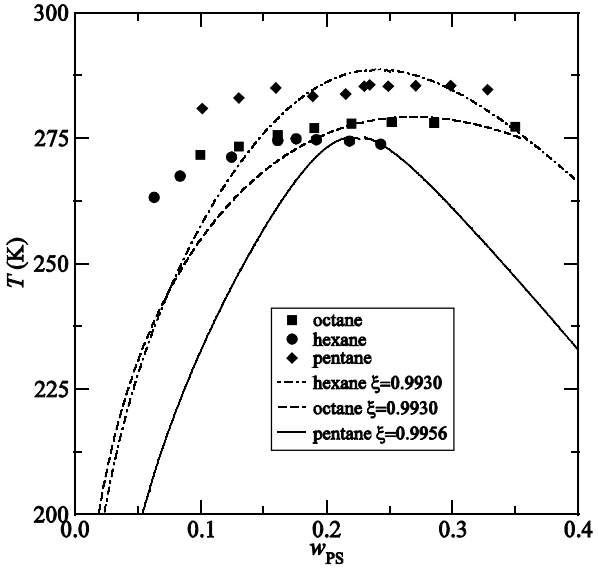

Figure III.3.11: Liquid-liquid equilibria of PS 1241 and pentane, hexane and octane. Experimental data from Imre and van Hook (2001).

It is worthwhile mentioning that while m, σ actually increase with the polymer´s molecular weight for polymer systems, the same is not true for the ε parameter. In the previous chapter, it was shown that when modeling polymer phase equilibria, the energy parameter for high molecular weight polymers is in fact lower than the expected when using an homologous series (Pedrosa et al., 2006). The model description and the changes in the polymer molecular parameters to accomplish phase equilibria modeling in Figure III.3.11 further support this fact. The energy parameter increases with molecular weight for very short polymers and then decreases again for high molecular weight polymers. This is probably due to the entanglement and agglomeration in the large polymer chains, which lowers the polymer energy.

III.3.3.3. Gas-liquid Equilibria

In the context of phase equilibria of polystyrene, the solubility of carbon dioxide was analyzed with the use of the soft-SAFT and PC-SAFT EoS's. Both data from Oliveira et. al at low pressure (Oliveira et al., 2004) and high pressure (Oliveira et al., 2006) were modeled and the results are presented in Figures III.3.12a and b. The molecular weight of

the polymer used is of 190000 g/mol. The molecular parameters for carbon dioxide were estimated in chapter III.4 for soft-SAFT (Pedrosa et al., 2005) and taken from literature for PC-SAFT (Gross and Sadowski, 2001), and are provided in Table III.3.2 for completeness. Figure III.3.12a shows the low pressure modeling of the solubility of carbon dioxide in polystyrene with the soft-SAFT and PC-SAFT EoS, without any binary interaction parameter. For high pressure solubility an interaction parameter is needed, as can be seen in Figure III.3.12b.

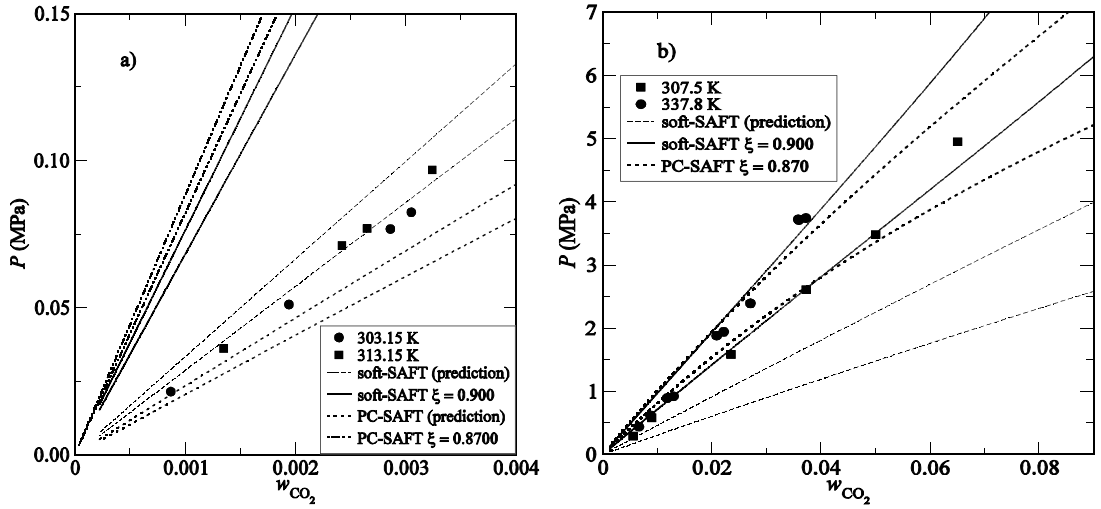

Figure III.3.12: (a) Low pressure solubility of carbon dioxide in polystyrene (Mn = 190000 g/mol) modeled with soft-SAFT and PC-SAFT. Data from Oliveira et. al (2004). (b) Solubility of carbon dioxide in polystyrene in the high pressure region modeled with the soft-SAFT and PC-SAFT models. Data from Oliveira et. al (2006).

Additionally, the description of the low pressure data with the soft-SAFT EoS using the binary parameter fitted to the high pressure data is shown in Figure III.3.12a. In Figure III.3.12b, the predicted solubility is shown for the soft-SAFT model, which is lower than the actual one. These results lead to the conclusion that some effect may be present in the high pressure region, namely polymer swelling, that the SAFT EoS cannot accurately describe. Apart from this underestimation of the high pressure phase equilibria, the tendency of the solubility of carbon dioxide in polystyrene is well described.

III.3.3.4. Conclusions

We have used two versions of the SAFT equation of state (soft-SAFT and PC-SAFT) to describe the rich behavior experimentally observed for polystyrene mixtures with several solvents. Both versions of the equation were able to accurately describe most of the features shown by these mixtures, including vapor-liquid, liquid-liquid and liquid/gas solubility data.

The molecular parameters of the pure polymers have been estimated following two different methods (Kouskoumvekaki et al., 2004a and Gross and Sadowski, 2002). The chosen method (Gross and Sadowski, 2002) was the one that provides the best results for the description of the polystyrene mixtures and it consists on fitting the polymer molecular parameters, along with the binary interaction parameters, to mixture data. Once the parameters of the pure polymers were obtained, they were used to model a series of polystyrene/solvent mixtures. These solvents range from aromatic compounds (benzene, ethylbenzene) to alkanes (nonane, pentane, hexane, octane, cyclohexane and methylcyclohexane) and esters (ethyl formate and isopropyl acetate) and water. Both models provide a good description of the VLE, GLE and LLE for the studied mixtures, being soft-SAFT superior in some cases.

III.4. Poly(ethylene glycol)

III.4.1. Introduction

Poly(ethylene glycol), along with the poly(ethylene oxide), belong to a family of polymers that exhibit very different thermodynamic properties according to the molecular weight. The low molecular weight members are viscous fluids or waxy solids while the high molecular weight ones are crystalline thermoplastics. This difference in behavior is mainly due to the importance of the hydroxyl end groups in the polymeric chain. Poly(ethylene glycol) is well known for its hydrophilicity, water-solubility, lack of toxicity and excellent biocompatibility. It has been combined physically or chemically with many therapeutic polymeric systems, either proteins, particles or implants to make them stealthy with respect to natural body defenses (Parveen and Sahoo, 2006; Osada and Kataoka, 2006 and Annunziata et al., 2002). It is also used in other fields such as in agriculture, wood processing and paint industry where it has an emulsifying role, and in batteries, chromatography and medicine as supporting agent (Sabadini, 1993).

Although poly(ethylene glycol) is found in a wide spread range of applications, the modeling of PEG mixtures phase equilibria still remains a challenging task due to its known associating behavior and also to the change in the polymer thermophysical properties with the molecular weight. The increasing complexity of polymer systems resulting from the development of new processes at extreme conditions (as for example where one of the components is supercritical) and/or the design of new materials for a specific need, where polymer architecture plays a dominant role, aggravate this situation. From a past situation where polymers were used in an almost pure state to the present situation where the polymeric material properties can be tailored to specification by formulation, polymer phase equilibria have increased in complexity but also in importance. Due to the large differences in the molecular sizes of polymer and solvents, to the polydispersity of polymers and to relative importance of the several groups within the polymers according to the polymer molecular weight, the phase behavior of polymer

systems is usually more complex than of systems of small molecules and thus requires the evaluation of the performance and robustness of models when they are used in polymer systems.

III.4.2. Modeling of Oligomers

III.4.2.1. Introduction

The use of ethyleneglycol (EG) and its oligomers such as diethylene glycol (DEG), triethylene glycol (TEG) and tetraethylene glycol (TeEG) has been increasing in industry for the past few years. Their main use is in the petroleum industry as an inhibitor of the formation of gas hydrates, due to their low vapor pressure and their high solubility in water. Another common use of ethylene glycols is as solvents for the selective removal of aromatic hydrocarbons from naphtha (Gupta et al., 1989). Thus, the knowledge of the vapor-liquid equilibria (VLE) behavior of the relevant mixtures of ethylene glycol oligomers in separation processes in which they are used is extremely important. In addition, it will help in the design of the optimal conditions of application of larger molecules, such as polyethylene glycol (PEG), from a fundamental point of view. Unfortunately, experimental data on these oligomer systems is rather scarce. In fact, based on current knowledge, no systematic study on the influence of chain length and/or molecular architecture on the solubility of different compounds has been performed up-to-date. In addition, the complexity of these mixtures presents a challenge to any modeling approach. Hence, it would be desirable to have a reliable theoretical tool in which the influence of these different variables can be checked.

In this work, a systematic study of the influence of the molecular architecture on the solubility of several compounds in EG oligomers from a modeling approach is performed. For this purpose we use the soft-SAFT equation (Blas and Vega, 1997; Blas and Vega, 1998 and Pamiès and Vega, 2001). A molecular model for each of the compounds is proposed. The molecular parameters are obtained by fitting to the available vapor-liquid equilibria data. Special care is taken on the meaning of the parameters and the possible transferability

of them. A correlation of the molecular parameters with the molecular weight of the compounds is proposed for EG oligomers, which can be transferred to long molecules, including polyethylene glycol (PEG) as it will be in the next section. The performance of soft-SAFT in describing VLE for mixtures is assessed by comparing its results with experimental data and/or with other thermodynamic models. Other molecular models used for comparisons were G^E based models (sUNIQUAC (Pedrosa et al., 2004)) and the Flory Huggins (FH) theory, which have proved to be accurate for complex mixtures. The Peng-Robinson EoS (Peng and Robinson, 1976) is also used for comparison, chosen as a benchmark equation because of its use as standard in process simulation on chemical industry. Since the Peng Robinson (Peng and Robinson, 1976) EoS is widely spread in the academic and industrial environments, we also use it here as a benchmark equation provided for reference. The equation can be written as:

$$P=\frac{RT}{V-b}-\frac{a\left(1-m\left(1-\sqrt{T_r}\right)\right)^2}{V(V+b)+b(V-b)} \tag{III.4.1}$$

where

$$a=0.45723553\frac{R^2T_c^2}{P_c} \tag{III.4.2}$$

$$b=0.07779607\frac{RT_c}{P_c} \tag{III.4.3}$$

$$m=0.37464+1.54226\,\omega-0.26993\,\omega^2 \tag{III.4.4}$$

being $T_r = T/T_c$ the reduced temperature, T_c and P_c the critical temperature and pressure of the given fluid, respectively, R is the universal gas constant and ω the Pitzer factor, which essentially takes into account the non-sphericity of the molecules. The equation can be applied to mixtures with the usual van der Waals one fluid theory, and mixing rules are applied as follows:

$$a=\sum_i\sum_j x_i x_j\sqrt{a_i a_j}\zeta_{ij} \tag{III.4.5}$$

$$b=\sum_i\sum_j x_i x_j\left[\frac{1}{2}\left(b_i+b_j\right)\right]\delta_{ij} \tag{III.4.6}$$

where the ζ_{ij} and δ_{ij} are the binary interaction parameters that are fitted to mixture data. Usually ζ_{ij} is represented by $(1-k_{ij})$ in most cases where the equation is used. We have used this particular notation for a straightforward comparison with soft-SAFT. Critical properties needed to use the PR EoS were taken from the NIST webbook (NIST, 2005) and the Pitzer factors were taken form the book published by Elliot and Lira (1999). In the case of the ethylene glycols, the determination of the Pitzer factor was taken from pure component vpor pressure data using the following expression:

$$\omega = \log P_r^{\sigma}|_{T_r=0.7} - 1.0 \qquad \text{(III.4.7)}$$

Finally, we use soft-SAFT with the molecular parameters obtained in this work to study the solubility of two selected systems, benzene and carbon dioxide, on different EG oligomers, as a function of their chain length. No comparisons with other refined versions of SAFT (Gil-Villegas et al., 1997 and Gross and Sadowski, 2001) are performed since, in principle, no qualitative differences should be expected with respect to soft-SAFT as applied to these type of mixtures. Only a slightly change on the the particular values of the EoS parameters depending on the equation used (i.e., the energy parameter has not an exact mapping in a square-well fluid and in a LJ fluid when representing the same real substance) would be expected.

III.4.2.2. Results and Discussion

The performance of the soft-SAFT EoS, as well as sUNIQUAC and FH methods for the description of EG, DEG, TEG and TeEG and the mixtures of EG+CO_2, EG+N_2, EG+C_6H_6; DEG+CO_2; TEG+C_6H_6, TEG+C_6H_{14}; TeEG+CO_2, TeEG+C_6H_6 is addressed in this subchapter. Experimental data for these mixtures was taken from different sources available in the literature (Gupta et al., 1989; Zheng et al., 1999; Jou et al., 2000; Rowley and Hoffma, 1990; Breman et al., 1994 and Yu et al., 1999). Experimental vapor-liquid equilibria (VLE) data was first used to fit the molecular parameters of the different pure compounds required by soft-SAFT and a correlation for the molecular parameters of EG

oligomers as a function of their molecular weight was established. These parameters were then used to check the accuracy of the soft-SAFT EoS for predicting the mixture behavior, as well as for searching trends in the solubility behavior as a function of the molecular weight and/or thermodynamic conditions.

III.4.2.2.1. Pure Components

The molecular parameters m, σ and ε for EG, DEG, TEG and TeEG, obtained by fitting the available VLE data (DIPPR, 1998) are presented in Table III.4.1.

Table III.4.1: Molecular parameters for the EG oligomers and other compounds used in their mixtures found by fitting with experimental data

Molecule	T range (K)	m	σ (Å)	ε/k_B (K)	ε_{HB}/k_B (K)	k_{HB} (Å^3)	Q (C m^2)	AAD (%)	ref
EG	270.0-470.0	1.751	3.668	326.05	4384	4195	-	1.13	DIPPR, 1998
DEG	280.0-475.0	2.548	3.860	334.40	4384	4195	-	2.74	DIPPR, 1998
TEG	300.0-610.0	3.190	4.010	340.58	4384	4195	-	4.18	DIPPR, 1998
TeEG	310.0-415.0	4.041	4.033	342.49	4384	4195	-	1.44	DIPPR, 1998
Carbon Dioxide	228.0-304.0	1.571	3.184	160.19	-	-	4.4×10^{-40}	1.00	NIST, 2005
Nitrogen	71.0-125.0	1.205	3.384	89.16	-	-	1.2×10^{-40}	0.80	NIST, 2005
Benzene	279.0-552.0	2.048	3.970	306.1	-	-	9.8×10^{-40}	2.70	NIST, 2005
Methane	95.0-170.0	1.000	3.728	172.2	-	-	-	-	Pamiès and Vega (2001)
Propane	100.0-350.0	1.776	3.811	219.5	-	-	-	-	Pamiès and Vega (2001)
Hexane	185.0-450.0	2.832	3.929	254.4	-	-	-	-	Pamiès and Vega (2001)

The association parameters (ε_{HB} and k_{HB}) were fitted to EG VLE data and their values were fixed for the rest of the oligomers. The maximum AAD was obtained for TEG (4.18%), being the other deviations well inferior to that value. In order to get visual information on the accuracy of these fittings, the experimental vapor pressure and density-temperature data for the four oligomers studied are plotted along with the description of the soft-SAFT model in Figures III.4.1a and III.4.1b, respectively. As shown in the figures the fitting is excellent, except near the critical point. This was expected, since we are using an analytical equation of state, in which the density fluctuations occurring near the critical region are not explicitly taken into account. Since we are not interested in the critical region, this fact does not affect the performance of the soft-SAFT EoS in this work.

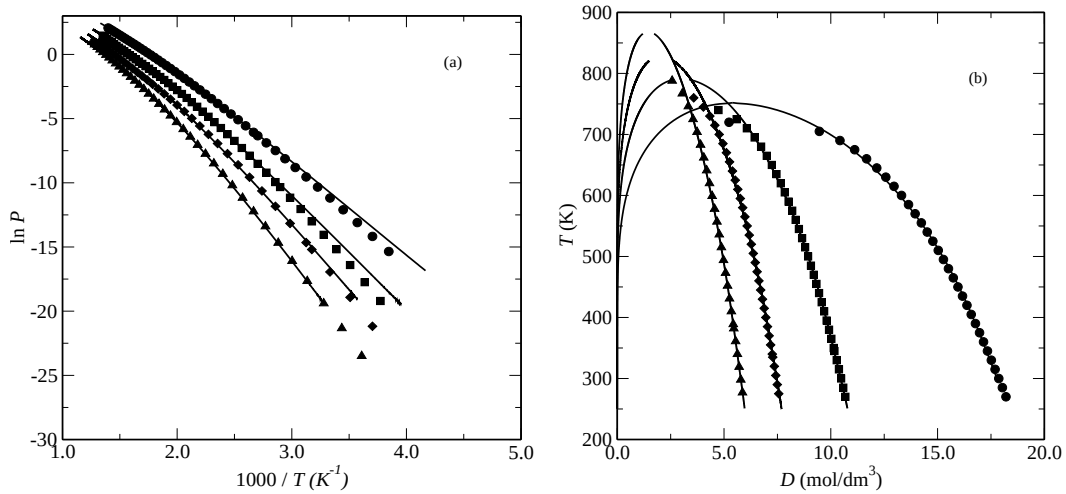

Figure III.4.1: (a) Logarithm of the vapor pressure versus the reciprocal of temperature and (b) vapor and liquid density as function of temperature of the ethyleneglycol oligomers (EG (●), DEG (■), TEG (◆) and TeEG (▲)). Symbols represent the experimental data (Zheng et al., 1999), while the line corresponds to the soft-SAFT modeling.

As previously done for the *n*-alkanes and perfluoroalkanes series (Pamiès and Vega, 2001 and Dias et al., 2004), the soft-SAFT parameters can also be correlated with the molecular weight (*Mn*) of the oligomers of ethylene glycol. These correlations are expressed in the following set of equations:

$$m = 0.698 + 0.017\, M_n \qquad \text{(III.4.8a)}$$

$$m\sigma^3 = 2.804 + 1.351\, M_n \qquad \text{(III.4.8b)}$$

$$m\varepsilon/k_B = 195.8 + 6.064\, M_n \qquad \text{(III.4.8c)}$$

Units of σ and ε/k_B are Å and K, respectively.

A graphical representation of equations III.4.8 is provided along with the optimized parameters in Figure III.4.2. The correlation coefficient for all curves is higher than 0.99, providing an excellent correlation for extrapolation purposes. An advantage of having parameters with physical meaning is that their physical trend can be investigated, not just the correlation (Pamiès and Vega, 2001). Note that when the linear correlation with the molecular weight is done the fluctuations of the parameters may be hidden by the multiplication by m and also by having σ^3 instead of σ. Although the molecular parameters are *effective* and we are using a crude model in which different groups are represented with the same σ and ε parameters, it is expected that they tend to a constant value, since the effect of the end-groups (associating ones) should become smaller compared to the rest of the chain as the chain length increases. A detailed discussion on the subject can be found in reference (Pamiès and Vega, 2001). Although not shown here for conciseness, we have observed that m, σ and ε follow the expected behavior. For instance, the value of m and ε are larger than in the corresponding alkanol, with the same number of CH_2 groups, comprising the specific interactions of the ether oxygen inside the molecule.

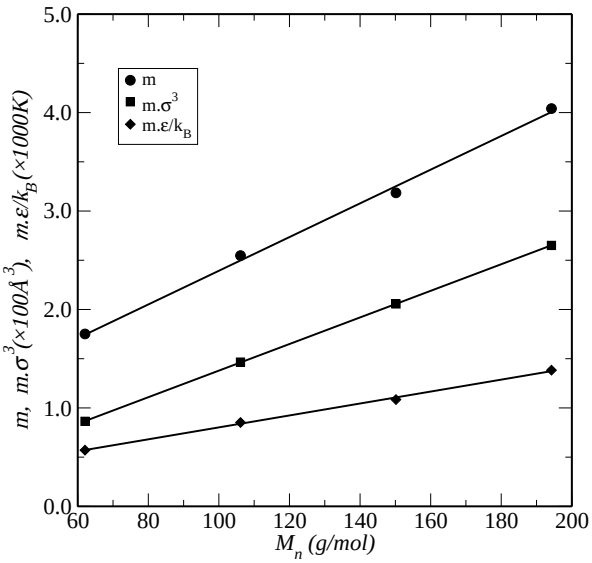

Figure III.4.2: Graphical representation of the correlation of molecular parameters m, $m\sigma^3$, and $m\varepsilon/k_B$ found for the ethylene glycol oligomers (equation III.4.8).

Since we are modeling EG oligomers in mixtures we also need the molecular parameters for the other components. The molecular parameters for methane, propane and *n*-hexane were taken from a previous work (Pamiès and Vega, 2001) and their values are also displayed in Table III.4.1. No molecular parameters were previously fitted with the soft-SAFT equation for N_2, benzene and CO_2 with quadrupole interactions; they have been obtained by fitting to the available VLE data within the present work with the molecular model outlined in the previous section. The values for the quadrupole moments Q for these molecules obtained from the fitting are in agreement with the ones present in literature (Benavides et al., 2000 and Bürgi et al., 2002). The carbon dioxide molecule is modeled as three segments one of which has the quadrupole ($x_p = 1/3$), the nitrogen is modeled as being composed by two segments and one as the quadrupole ($x_p = 1/2$) and finally benzene is modeled has a set of six segments in a radial disposition and the quadrupole is assumed to be present in one of these segments ($x_p = 1/6$). The molecular parameters estimated are also reported in Table III.4.1.

III.4.2.2.2. Mixtures:

Once the molecular parameters of the pure components are available, soft-SAFT can be used to study the behavior mixtures of EG oligomers with other compounds. A comparison with G^E models for two selected systems TEG-*n-hexane* and TeEG-benzene, is reported. The solute chosen were n-hexane and benzene. This choice was based on the experimental systems available and although, they present similar interactions (one associating fluid mixed with one which is not), their behavior in terms of vapor-liquid equilibria is quite different as it will be discussed later.

The data for mixtures of ethylene glycols with non-associating components are very scarce in the open literature. Only a few systems could be found. In fact, as we have mentioned in the introduction, to our knowledge, this is the first time a systematic study of the solubility of different compounds on EG and its oligomers is performed. The experimental measurements found for the mixtures of the glycols investigated here come in

various formats, that is, they are published as isobars, isotherms or isopleths. A great advantage of using a molecular-based equation is that once the molecular parameters of the pure compounds and the binary parameters at some selected conditions are fitted, the equation permits to perform a fair comparison of the different compounds *at the same thermodynamic conditions*, as well as the influence of the molecular architecture in the phase behavior of the mixtures.

For the EG oligomers systems, we have decided to use only one binary parameter for both the soft-SAFT equation and the PR equation, for all mixtures investigated. This is fair in terms of accounting for deviations from the ideal behavior with just one parameter, but it provides larger deviation values from unity than in the case where two binary parameters, separating size and energy deviations are explicitly considered. The chosen parameter has been that related to the energy of interaction (ξ_{ij} and ζ_{ij}, respectively).

Mixtures of ethylene glycol

The mixtures under study are three: EG with carbon dioxide, nitrogen and methane. The experimental data for these mixtures have been taken from (Zheng et al., 1999). Results obtained from soft-SAFT are displayed as full lines in Figures III.4.3, III.4.4 and III.4.5, respectively, along with the experimental data (symbols). We have obtained the binary parameter at one temperature and use the soft-SAFT in a predictive manner for the other temperatures presented in these figures. The values of the binary interaction parameters were obtained at the lowest temperature, 323.15 K, for the mixtures of EG with carbon dioxide (ξ_{ij}=0.8321) nitrogen (ξ_{ij} = 0.5188) and methane (ξ_{ij} = 0.6665). Figures III.4.3 to III.4.5a also show predictions obtained with the soft-SAFT EoS if no binary parameters are used. Large deviations from the experimental data are observed in all cases for pure component predictions. This is due to the high asymmetry of the systems, but it also shows how good the soft-SAFT model behaves when using just one temperature independent binary interaction parameter. The overall performance of the soft-SAFT equation for all three mixtures is quite good. Regarding the behavior of the three mixtures considered, the solubility decreases from CO_2 (most soluble), to nitrogen and methane,

which requires higher pressures at the same temperature to be dissolved in EG. A similar behavior was observed by Wiesmet et al. (2000) for mixtures with PEG and CO_2, nitrogen and propane. For the EG/ CO_2 mixture, soft-SAFT is able to capture the change in the solubility behavior of CO_2 in EG with pressure at the three temperatures considered.

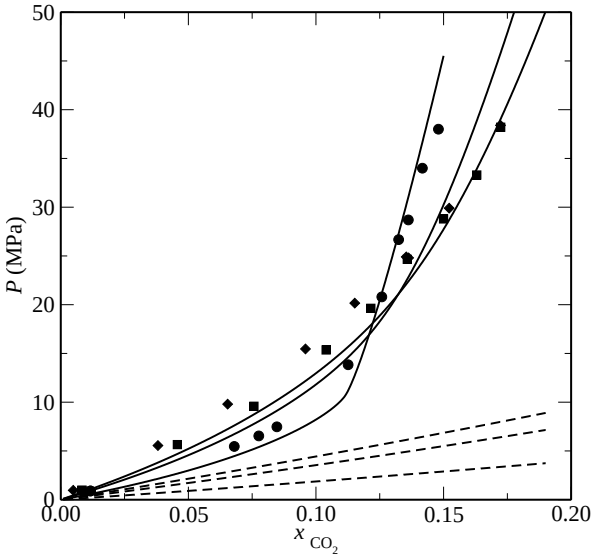

Figure III.4.3: Isotherms for the mixture of ethylene glycol with carbon dioxide. Full line: soft-SAFT with one adjusted binary parameter, dashed line: soft-SAFT predictions without binary parameters. Symbols: experimental data from (Zheng et al., 1999) at different temperatures: circles (323.15K), squares (373.15K) and diamonds (398.15K).

We have focused on the mixture EG with methane to compare the performance of the two equations of state models used in this work. For this system, a study with G^E based models cannot be made as the pressure is very high, i.e. far from the applicability of these models, which are valid only at pressures close to atmospheric.

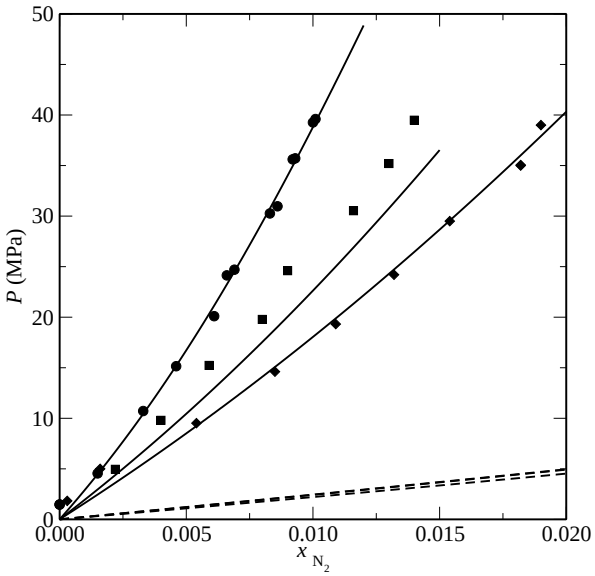

Figure III.4.4: Isotherms for the mixture of ethylene glycol with nitrogen (legend as in Figure III.4.3)

The study with Peng Robinson (PR) EoS and its performance is compared with soft-SAFT's in Figures III.4.5a and III.4.5b. Two comparisons are made: in the first case the binary interaction parameter of both EoS's is kept *independent of temperature* (ξ_{ij} = 0.6665 for soft-SAFT and ζ_{ij} = 1.0109 for PR), fitted at 323.15K (Figure III.4.5a), while in the second case the binary parameter is fitted for each temperature (Figure III.4.5b). The temperature dependent parameters used in Figure III.4.5b are presented in Table III.4.2. Note that for this particular case the binary parameter in the soft-SAFT equation deviates considerably more from unity than the corresponding value in the Peng Robinson EoS. However, the soft-SAFT parameter shows less dependence with temperature than the Peng Robinson one. As expected, both equations perform well if the binary parameters are fitted at each temperature (Figure III.4.5b), but in this case both models lose their extrapolative power.

Table III.4.2: Binary parameters for the soft-SAFT and PR EoS for the ethylene glycol + methane mixture for each temperatures (Figure III.4.5b)

T (K)	ξ_{ij}	ζ_{ij}
323.15	0.6665	1.0109
373.15	0.6344	0.9228
398.15	0.6426	0.8968

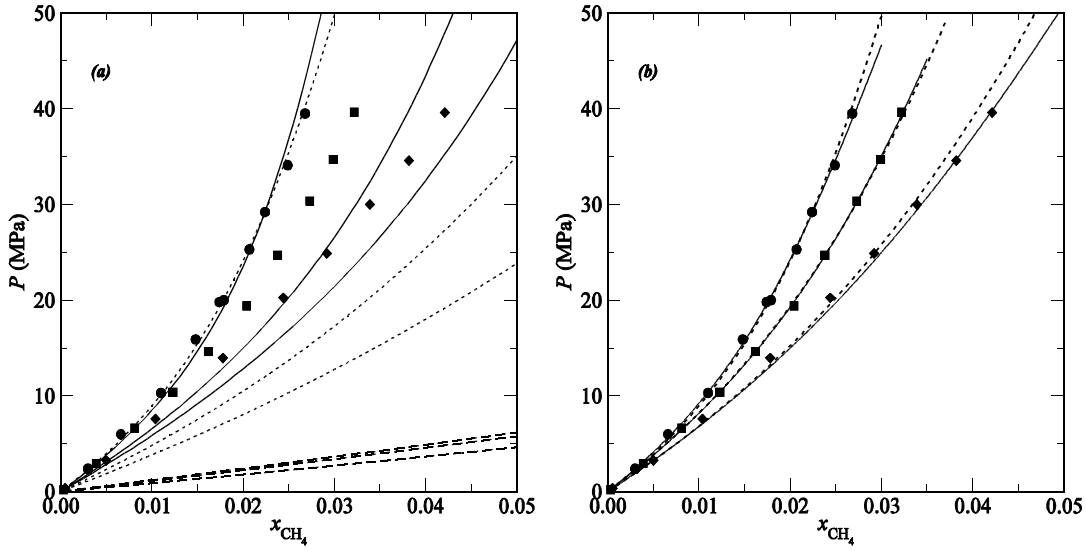

Figure III.4.5: Isotherms for the mixture of ethylene glycol with methane using PR and soft-SAFT EoS. (a) Dashed lines: soft-SAFT predictions without binary parameters; full lines: soft-SAFT with one binary parameter (ξ_{ij} = 0.6665); dotted line: PR with one fitted binary parameter (ζ_{ij} = 1.0109); both fitted to T=323.15 K. (b) Performance of the soft-SAFT (full lines) and PR (dotted lines) EoSs when the binary parameter is fitted as a function of temperature. Symbols as in Figure III.4.3.

Mixtures of diethytlene glycol

Only one mixture of DEG with carbon dioxide was found in the literature (Jou et al., 2000). The performance of the soft-SAFT equation with the molecular model described before is shown in Figure III.4.6. As in the previous case, the quadrupole interactions in the CO_2 molecules have been explicitly considered. Figure III.4.6a depicts the performance of the soft-SAFT equation when the binary parameter is fitted to the intermediate temperature (348.15K) and used to predict the behavior of the mixture at different temperatures.

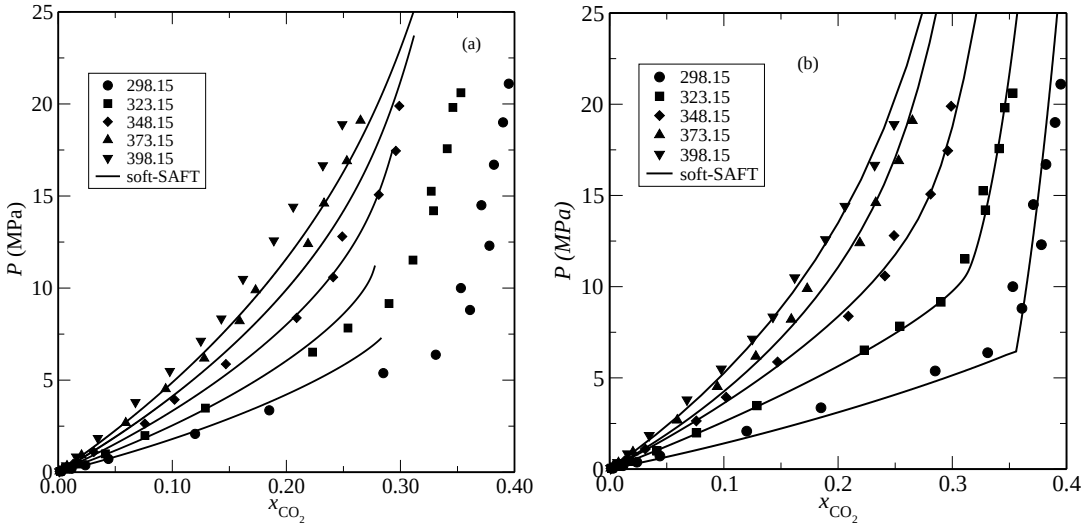

Figure III.4.6: The di-ethylene glycol / CO_2 binary mixture. (a) single binary parameter ξ_{ij} = 0.8935, and (b) a binary parameter for each T (Table III.4.3). Lines: soft-SAFT model, symbols: data from literature (Jou et al., 2000).

Although the equation is able to capture the behavior of the mixture in all cases, predictions deteriorate as one deviates from the fitted temperature, and also as the molar fraction of carbon dioxide increases. The performance of the equation can be improved if the binary parameters are fitted to each temperature, as shown in Figure III.4.6b. The temperature dependent parameter values for Figure III.4.6b are provided in Table III.4.3. Note that the dependence of this parameter on temperature is very weak, and it seems to reach an asymptotic value at high temperatures. This limiting value could be use to predict the behavior of the mixture at different temperatures, without further fitting.

Table III.4.3: soft-SAFT binary parameters used in Figure III.4.6b

T (K)	298.15	323.15	348.15	373.15	398.15
ξ_{ij}	0.9237	0.9085	0.8935	0.8852	0.8857

It should be emphasized that this is a very challenging mixture, not only in terms of the components integrating it, but also for the thermodynamics conditions at which the system is investigated. The equation performs very well under these conditions (especially when a temperature dependent binary parameter is considered), being able to detect a possible

phase split at 298.15K and an approximate pressure of 6 MPa. Although this phase split was not mentioned in the original article from which the data was taken, it is possible that this may occur at temperatures below (and nearby) the critical temperature of CO_2. In fact, the equation follows the trend the experimental data presents at high pressures and low temperatures as well.

Mixtures of triethytlene glycol

Mixtures of TEG / benzene (Gupta et al., 1989) and TEG / *n*-hexane (Rowley and Hoffma, 1990) were found in literature and modeled with the soft-SAFT EoS. The mixture of TEG with benzene is rather symmetrical, and hence most models should describe it accurately. The experimental *T,x* phase diagram at 0.1 MPa taken from the literature (Gupta et al., 1989) is plotted together with the soft-SAFT model in Figure III.4.7. For this system the binary interaction parameter was not necessary when the quadrupole interactions are explicitly considered, since agreement with the experimental data is excellent. As a reference, the results obtained without the inclusion of the quadrupole are also shown in Figure III.4.7. In this case, a binary parameter would be needed to obtain the same accuracy as the one obtained with the quadrupolar term.

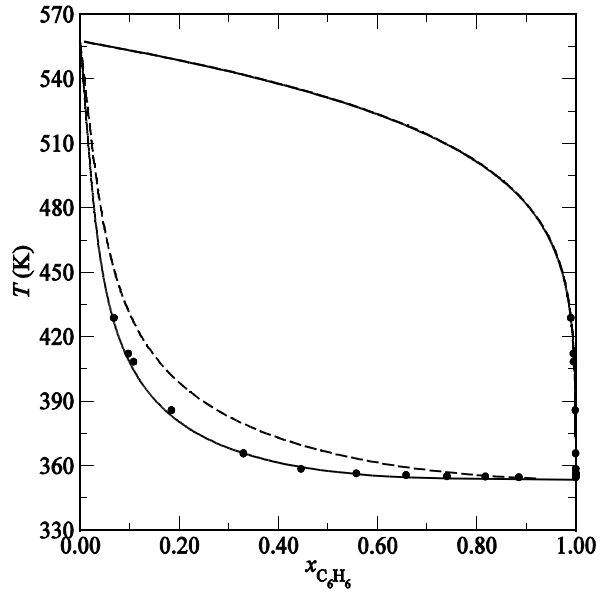

Figure III.4.7: Isobaric phase diagram for the TEG / benzene mixture. Full line soft-SAFT predictions with quadrupolar interactions included, dashed line predictions from the original soft-SAFT equation. See text for details. Symbols: data from literature (Gupta et al., 1989).

Concerning the mixture of TEG with *n*-hexane at 473 K, there is an important difference when the binary parameter is adjusted, as shown in Figure III.4.8a with the (black) full lines. The binary parameter used in this case was ξ_{ij}= 0.9690. This system is also studied with the PR equation, with ζ_{ij} = 0.9220. The results are shown in Figure III.4.8a in (red) full line. The dashed line corresponds to predictions from pure component parameters for both soft-SAFT (black dashed line) and PR (red dashed line) EoS's. It can be observed in the figure that a possible third phase forms at high composition of *n*-hexane, as the experimental data seems to flatten out for hexane mole fractions above 0.3. In this region, both the EoS models show phase instability. This is a very common situation when fitting a model to alkane/alcohol experimental systems (Englezos et al., 1989). The problem can be solved by fitting the binary parameters with the constraint of stability, given by the following stability function (SF):

$$SF = \frac{\partial \ln f_1^L}{\partial x_1} > 0 \qquad \text{(III.4.9)}$$

which has been described in the literature (Englezos and Kalogerakis, 1993). Here f_1^L stands for the fugacity of the liquid phase and x_1 for mole fraction of component 1 in the

liquid phase. The binary parameter found using this procedure was ξ_{ij} = 0.9429, for the soft-SAFT (black dashed-doted line) and ζ_{ij} = 0.9560 for the PR (red dashed-doted line), very close to each other and not too far from the unity value. Results are shown in Figure III.4.8a. In this case, the phase instability cannot be avoided without having a large deviation from the experimental data. It should also be noticed that in all cases the performance of the PR EoS is somewhat worse than soft-SAFT's, especially in the region where model instability is present.

Figure III.4.8b shows the study carried out with the G^E models for the TEG/ *n*-hexane mixture. As in the soft-SAFT equation, the binary parameters for the two models were obtained by fitting to this data. For the sUNIQUAC model the *two binary parameters* values were a_{12} = 1.08 J/mol and a_{21} = -0.08 J/mol, while the fitted value for the Flory-Huggins model was χ = 1.905. It possible to see that these two models studied show no tendency to have instability with the fitted parameters, but they also show a great deviation from experimental data compared to soft-SAFT, especially the Flory-Huggins model which clearly has a wrong tendency.

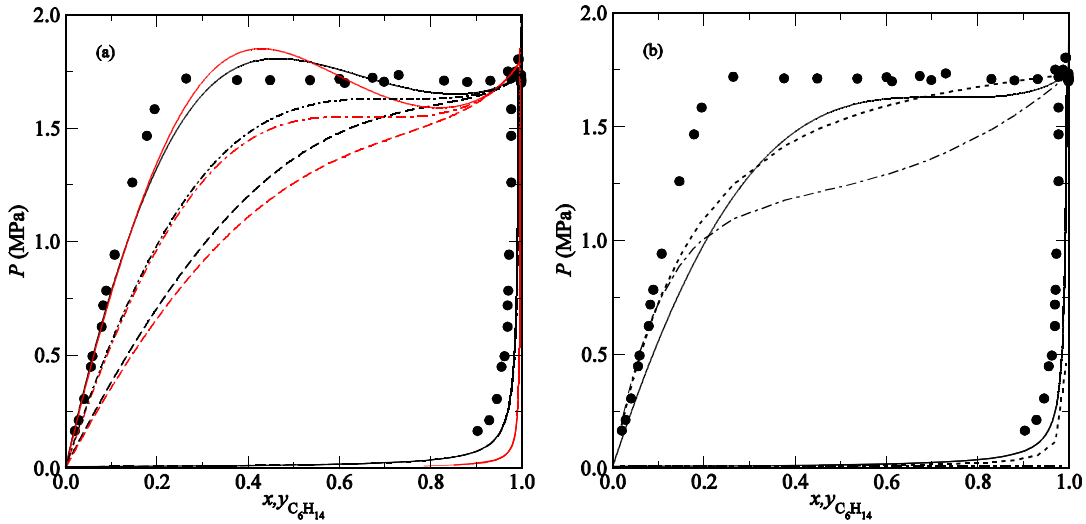

Figure III.4.8: Isothermal vapor liquid equilibrium of the mixture of TEG with hexane. (T = 473.15 K). (a) Black color represents soft-SAFT and red lines represent PR. Full lines and dashed lines represent both EoS's with and without fitted binary parameters, respectively, dashed-dotted line: both models fitted to the limit of stability. (b) full line: soft-SAFT in the stability limit, dotted lines: sUNIQUAC and dashed-dotted: Flory Huggins model. Symbols: data from literature (Eowley and Hoffma, 1990).

Mixtures of tetraethylene glycol

Only two mixtures were found for TeEG: TeEG / carbon dioxide (Breman et al., 1994) and TeEG / benzene (Yu et al., 1999). The experimental data for the TeEG/carbon dioxide (Breman et al., 1994) mixture is the only one presented in the form of isopleths in the original article. In this case the composition of carbon dioxide in the liquid phase was kept constant and it was equal to 0.08. Figure III.4.9 shows the soft-SAFT results when modeling this system with and without the binary interaction parameter. As in some of the previous mixtures, the pure component parameters are able to qualitatively capture the shape of the curve, but if one is interested in quantitative results the binary parameter is needed. The binary interaction parameter found was ξ_{ij} = 0.8980. Once again, a small change (about 12%) in the binary interaction parameter produces a relevant change in the model behavior, in the order of 40%.

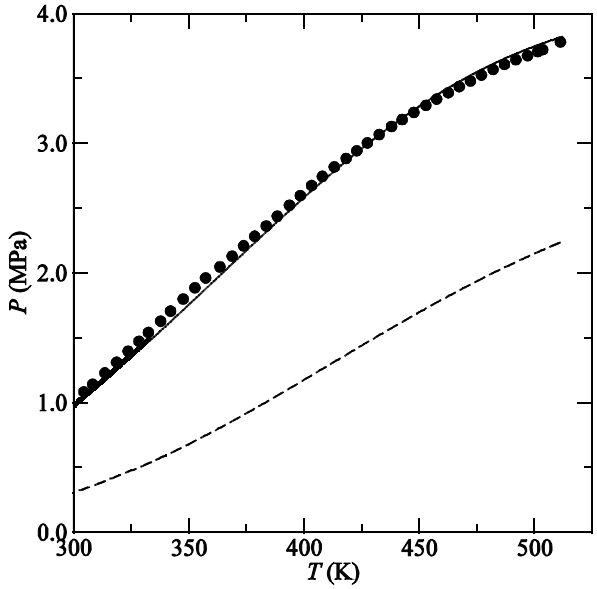

Figure III.4.9: Mixture of TeEG and carbon dioxide at a fixed composition of CO_2 of 0.08. Full line and dashed line are soft-SAFT with and without a binary parameter, respectively, symbols: data form literature (Breman et al., 1994).

As for the case of TEG, predictions with soft-SAFT for the mixture of TeEG with benzene (Yu et al., 1999) at 0.1 MPa, show almost no deviations to the experimental data. This can be explained by the symmetry of these systems compared to the ones where a gas,

like carbon dioxide or nitrogen is present. Figure III.4.10a presents predictions obtained with the (polar) soft-SAFT and the results obtained with the PR EoS's with (ζ_{ij} = 0.9402) and without the binary interaction parameter. Figure III.4.10b shows how G^E based models compare with soft-SAFT for this mixture. In this case all models perform reasonably well since this is a system with no asymmetries. Both equations of state, soft-SAFT and PR, perform similarly, with or without the binary interaction parameter.

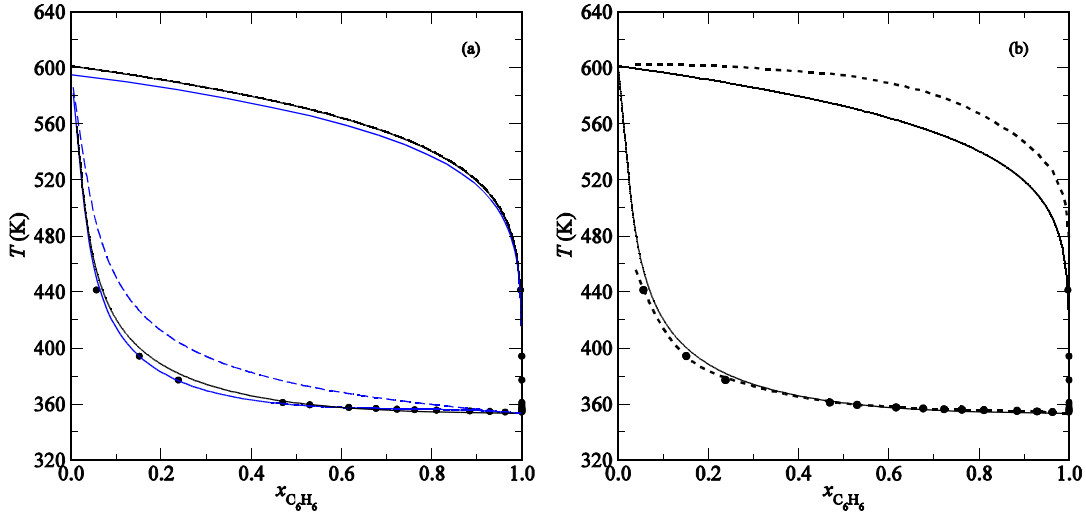

Figure III.4.10: Description of the TeEG / benzene mixture at 0.1 MPa (a) blue dashed line: predictions from PR; full line: quadrupolar soft-SAFT predictions; blue full line: PR with a binary parameter (b) full line: quadrupolar soft-SAFT predictions; dotted line: sUNIQUAC with two binary parameters. Symbols: experimental data from literature (Yu et al., 1999).

The G^E model (sUNIQUAC, a_{12} = 1.93 J/mol, a_{21} = 0.250 J/mol) also performs well for the liquid compositions (its parameters were adjusted to this data) but there is some overprediction of the bubble point temperature: about 5% from the values given by PR and soft-SAFT. Note, however, that for this system there is no available data for lower compositions of benzene, only a few data points for higher compositions, hence, the vapor phase predictions should be taken with caution.

III.4.2.3. Influence of the molecular architecture on the solubility

So far we have performed a systematic check on the description of EG oligomers mixtures with the soft-SAFT EoS as well as with other thermodynamic models. Soft-SAFT has proved to be accurate and with good extrapolative power only with one temperature independent parameter in most of the cases. The next step is to use the equation to check the influence of the molecular architecture on the solubility of different compounds in EG oligomers. In particular, the influence of the chain length and the effect of breaking (or not) hydrogen bonds when solubilizing non-associating compounds in EG oligomers will be addressed.

EG, DEG, TEG, TeEG and PentaEG in benzene

It is of great interest to check the soft-SAFT predictive capability to describe the VLE for other mixtures. Hence, a VLE prediction of the systems EG / benzene, DEG/ benzene and PentaEG/ benzene at 0.1 MPa is made here for comparative purposes. Calculations are performed with the molecular parameters of the pure components. Based on the results presented no binary parameters are needed for these mixtures.

Soft-SAFT EoS predictions showing the effect of the chain length on the solubility of EG, DEG, TEG, TeEG and PentaEG on benzene at 0.1MPa are shown in Figure III.4.11. It is worth of noting that while the dew points are strongly dependent on chain length, the boiling points seem to be independent of the chain length, except for the EG/ benzene mixture. Note also that the differences in the dew points show an almost constant increase with chain length, a direct consequence of the increase vapor pressure value of the pure components with chain length.

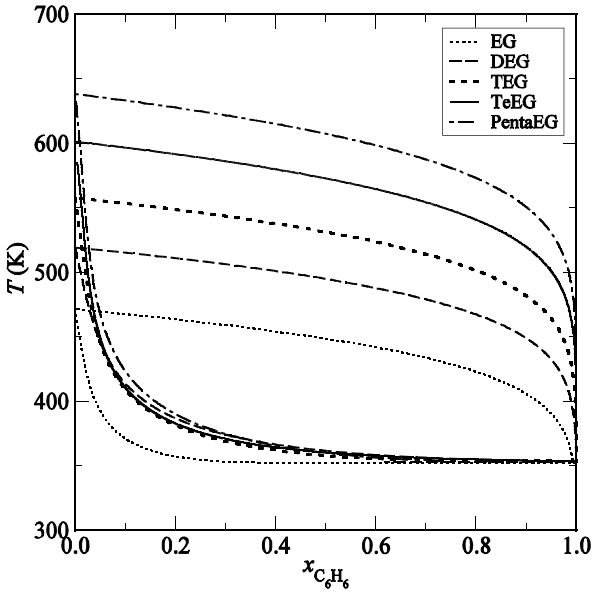

Figure III.4.11: The influence of the chain length on the solubility of benzene in EG, DEG, TEG and TeEG at 0.1MPa, as obtained from the soft-SAFT model.

EG, DEG, TEG, TeEG and PentaEG in carbon dioxide

Soft-SAFT is also used to study the influence of the chain length on the solubility of carbon dioxide in the EG oligomers (from EG to PentaEG). The molecular parameters for PentaEG have been obtained from equation III.4.8. The binary parameter for all mixtures was set to 0.88. This value lays between those fitted to the EG and TeEG mixtures with CO_2, and it is also very close to the limiting value of the temperature dependent parameter for the DEG/ CO_2 mixtures.

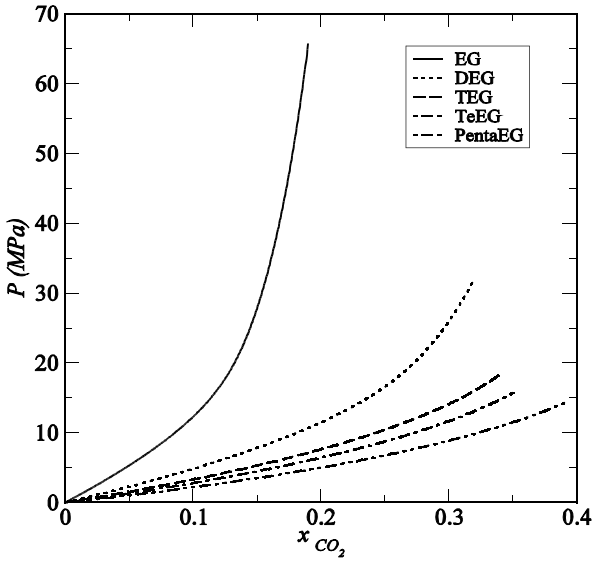

Figure III.4.12: The influence of the chain length on the solubility of carbon dioxide in EG, DEG, TEG, TeEG and PentaEG as predicted from the soft-SAFT EoS at 373.15K

Figure III.4.12 shows how the influence of the molecular architecture (chain length) is remarkable in this case, the solubility increases as the chain length increases, and changes are quite more significant for the shorter molecules. This may be explained by the fact that EG and DEG need to break hydrogen bonds to solubilize CO_2; as the chain length increases, the solubility is achieved without hydrogen bonding breaking, being favored by the van der Waals interactions between the alkyl groups inside the chain and the CO_2 molecules. The ability to accommodate the CO_2 molecule within the non hydrogen bonding part of the molecule explains why the differences in solubility of CO_2 become smaller as the chain length of the EG oligomers increases. Wiesmet et al. (2000) have also observed a similar effect, although less noticeable: they measured the influence of the molecular weight of PEG on the solubilization of CO_2, obtaining a different behavior for the lightest compound, and no influence of chain length for the rest of the polymers investigated. The deviations were attributed to the influence of the chain ends in the shortest polymer, although it was not quantified.

III.4.2.4. Conclusions

We have developed a molecular model for the EG oligomer series within the context of the soft-SAFT approach. Molecular parameters were obtained by fitting to available experimental data for the VLE of pure components, ranging from EG to TeEG. It was possible to propose a correlation of the chain length, size and energy of interaction parameters with the molecular weight of the compounds, while the association parameters were fixed in all cases. This provides transferable parameters for the series and also for longer molecules, such as poly(ethylene glycol). The quadrupolar interactions have been explicitly considered for the case of CO_2, nitrogen and benzene. Although this has no effect on the pure component description, the inclusion of this interaction remarkably improves the description of the mixtures.

The use of the soft-SAFT equation allows a systematic study of the influence of different variables (chain length and thermodynamic conditions) on the solubility of several compounds in ethylene glycols. We have used available experimental data of some mixtures to fit one binary parameter of the soft-SAFT EoS to a given temperature, and use this parameter in a predictive manner for the rest of the temperatures. It has also been shown that a temperature dependent parameter improves the description in some cases. Once all needed parameters were obtained, soft-SAFT permits the study of the influence of the chain length on mixtures of EG oligomers with other compounds, at the same temperature and/or pressure. We have observed that when solubilizing a liquid-like solvent (benzene) the influence of the chain length is more noticeable in the dew point, while almost no effect is observed in the boiling point, except for the shortest member of the series, EG. On the contrary, the solubility of carbon dioxide on these oligomers strongly depends on chain length, since the breaking of hydrogen bonds in the EG and DEG is clearly harder for these oligomers.

Finally, the performance of the soft-SAFT equation for two compounds and two oligomers has been compared with other well-established thermodynamic models: G^E based models and the PR equation. G^E models are as accurate as the rest of the models

employed here for the TeEG/benzene mixture but for the TEG/*n*-hexane mixture the Flory Huggins model shows some difficulties in describing this system in a sound manner. Soft-SAFT provides better predictions than PR with a temperature independent binary parameter, while both models perform similarly if a temperature dependent binary parameter is used. This acts in favor of the extrapolative power of a molecular-based EoS versus most traditional equations.

III.4.3. Polymer modeling

The phase behavior of poly(ethylene glycol) oligomers up to tetra(ethylene glycol) in several solvents using soft-SAFT was already addressed above. Here, this study will be extended to higher molecular weight compounds and to a variety of solvents, which lead to rich phase equilibria behavior, usually of type IV or V in the classification of Scott and van Konynenburg (1970). These types of equilibria exhibit Lower and Higher Critical End Points due to the large differences, mainly size differences but often also energy differences, between the solvent and the polymer. In practical terms this leads to liquid-liquid phase equilibria exhibiting an Upper Critical Solution Temperature (UCST), mainly driven by the differences in energy and/or a Lower Critical Solution Temperature (LCST) conditioned by the difference in size of the components.

III.4.3.1. Polymer parameters

One of the most important issues related with the calculation of phase equilibria of polymer mixtures is the estimation of the molecular parameters of the equation of state for the pure polymer. In this work, the molecular parameters for poly(ethylene glycol) are found by using the correlation developed above for the series of ethylene glycol oligomers. It is represented by Equations III.4.8. The association scheme used assumes that only the end hydroxyl groups associate with other chains of polymer or solvent. This is in

agreement with the work of Crupi et al. (1995) Who studied the associating interactions present in pure liquid ethylene glycols (including several PEG polymers of low molecular weight) using Rayleigh wing and Fourrer transform infrared (FTIR)spectroscopies. They concluded that in liquid ethylene glycol all of the O-H groups are involved in the formations of hydrogen bonds. This behavior is similar to the one observed for n-alkanols, by the same authors (Crupi et al., 1995). It also was observed that intramolecular interactions in PEG of molecular weights of 200 and 2000 were of a very low probability. This means that, for reasons of polymeric steric hindrance these intramolecular interactions can be neglected. In fact, the existence of ring associating structures cannot be modeled in the TPT1 context, as discussed in the reviews on SAFT (Economou, 2002 and Müller and Gubbins, 2001). Accordingly, poly(ethylene glycol) is modeled assuming that only the end hydroxyl groups are able to associate with other chains of the polymer or solvents. This has already proved to be a good assumption in the description of the solubility of gases in poly(ethylene glycol) (Wiesmet et al., 2000).

III.4.3.2. Results and discussion

The data available for binary poly(ethylene glycol) mixtures is surprisingly scarce. The vapor-liquid equilibrium data focuses essentially on the solubility of gaseous compounds such as nitrogen (Wiesmet et al., 2000), propane (Wiesmet et al., 2000) carbon dioxide (Wiesmet et al., 2000 and Daneshavar et al., 1990). Some data also exists on the solubility of associating compounds lower alcohols such as such as methanol (Kim et al., 1999), ethanol (Kim et al., 1999) and 2-propanol (Zafarani-Moattar and Yeganeh, 2002) and water (Herskowitz and Gottlieb, 1985). In the case of liquid-liquid phase equilibria data for poly(ethylene glycol) / tert-butyl acetate from Saeki et al. (1976), and for mixtures of aromatics such as toluene, ethylbenzene and n-propylbenzene were reported by Sabadini (1993). Despite the limited data available, the resulting phase behavior is quite rich. In the next sections we will attempt to describe the same behavior with the soft-SAFT model, trying to highlight the molecular interactions leading to the macroscopic behavior.

The soft-SAFT description of poly(ethylene glycol) was accomplished by using the series of ethylene glycol oligomers studied above. The molecular parameters correlation developed based on that series is here reported for completeness:

$$m = 0.698 + 0.017 M_n \quad \text{(III.4.10a)}$$

$$m\sigma^3 = 2.804 + 1.351 M_n \quad \text{(III.4.10b)}$$

$$m\varepsilon/k_B = 195.8 + 6.064 M_n \quad \text{(III.4.10c)}$$

where *Mn* is the number molecular weight of the polymer.

The molecular parameters of the soft-SAFT EoS for the solvents used in this work are presented in Table III.4.4.

Table III.4.4: Molecular Parameters of the soft-SAFT EoS for non-polymer compounds

Compound	m	σ (Å)	ε/k_B (K)	Q (C m^2)	k_{HB} (Å^3)	ε_{HB}/k_B (K)	Reference
2-propanol	2.003	3.831	224.9	-	3450	2250	this work: data from DIPPR, 1998
benzene	2.048	3.970	306.1	9.80x10^{-40}	-	-	Blas, 1999
carbon Dioxide	1.571	3.184	160.19	4.40x10^{-40}	-	-	Pedrosa et al., 2004
ethanol	1.740	3.635	234.8	-	3387	2641	Pamiès, 2001
ethylbenzene	2.644	4.061	307.1	9.80x10^{-40}	-	-	this work: data from DIPPR, 1998
methanol	1.491	3.375	220.4	-	3213	4847	Pamiès, 2001
n-propybenzene	2.886	4.126	309.8	9.80x10^{-40}	-	-	this work: data from DIPPR, 1998
nitrogen	1.205	3.384	89.16	1.20x10^{-40}	-	-	Pedrosa et al., 2004
propane	1.776	3.811	219.5	-	-	-	Pamiès, 2001
tert-butyl acetate	3.209	3.815	261.84	-	-	-	this work: data from DIPPR, 1998
toluene	2.374	4.013	305.2	9.80x10^{-40}	-	-	this work: data from DIPPR, 1998
water	1.000	3.190	408.5	-	2367	2707	Blas, 1999

III.4.3.2.1. Vapor-liquid equilibria

The modeling of the solubility of carbon dioxide in PEG 400, 600 and 1000 g/mol, using the experimental data from Daneshvar et al. (1990) at 323 K is displayed in Figure III.4.13. Note that for this system the carbon dioxide is close to or in the supercritical state. A binary interaction parameter close to unity was used (ξ_{ij} = 0.9700) for all molecular weights. However, for the poly(ethylene glycol) with a molecular weight of 400 g/mol, this binary interaction parameter was not good enough to model the solubility of carbon dioxide in poly(ethylene glycol).

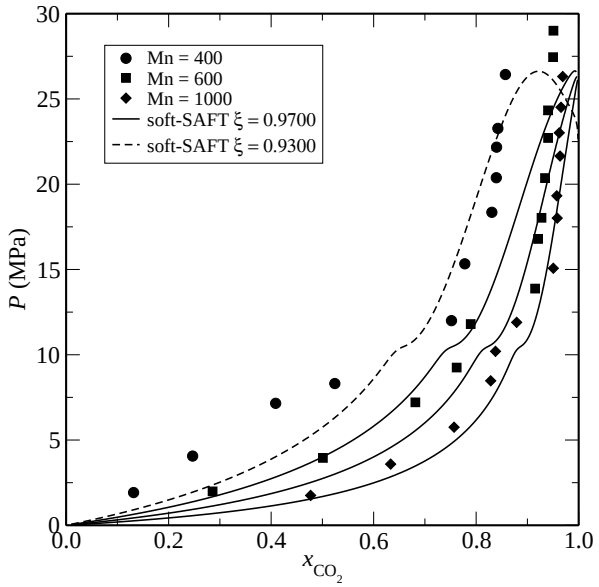

Figure III.4.13: Phase equilibria description by the soft-SAFT EoS of the solubility of carbon dioxide in poly(ethylene glycol) of molecular weights of 400, 600 and 1000 g/mol at 323.0 K in which the experimental data was taken from Daneshvar et al. (1990).

As shown in Figure III.4.13 a different binary interaction parameter was fitted to the solubility data for the polymer of 400 g/mol. We have also modeled the phase equilibria for the mixture poly(ethylene glycol) 1500 g/mol / carbon dioxide from Wiesmet et al. (2000) and for the polymers of 400 and 600 g/mol at other temperature from Daneshvar et al. (1990), obtaining similar results to those presented in Figure III.4.13. For the sake of shortness and clarity these results are provided as additional information, in appendix C.

The experimental solubility data from Wiesmet et al. (2000) of propane in poly(ethylene glycol) was also modeled using the soft-SAFT EoS. In the present case, the molecular weight of the polymer ranges from from 200 g/mol to 8000 g/mol. The results are displayed in Figure III.4.14 for the polymers with molecular weight of 200 and 8000 g/mol, and it shows the excellent performance of the soft SAFT model in the description of the temperature dependence of the equilibria, especially for temperatures higher than the critical temperature of propane.

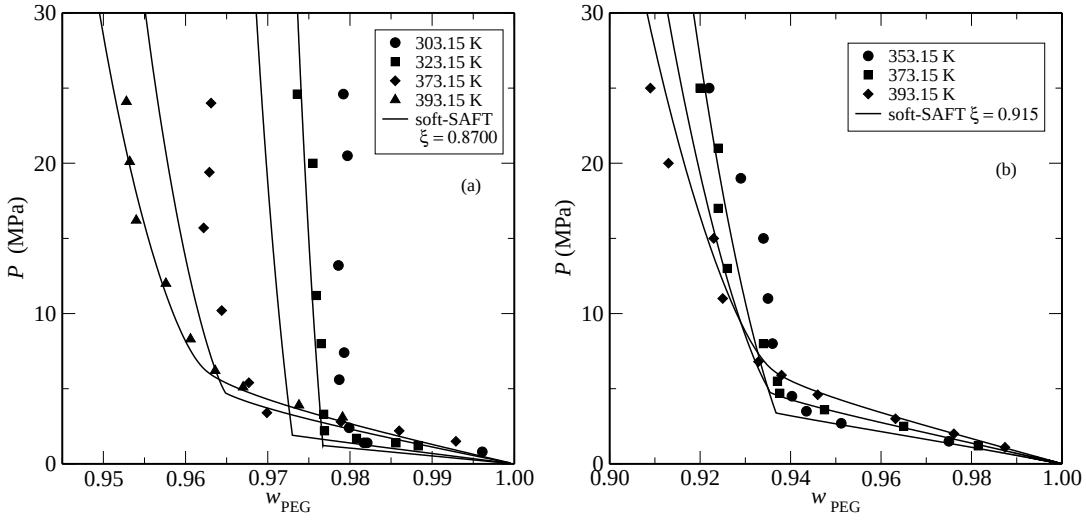

Figure III.4.14: Solubility of propane in poly(ethylene glycol) at four different temperatures as described by the soft-SAFT EoS. Experimental data from Wiesmet et al. (2000). a) poly(ethylene glycol) with a molecular weight of 200 g/mol and a soft-SAFT binary interaction parameter ξ_{ij} = 0.870. b) poly(ethylene glycol) with a molecular weight of 8000 g/mol and a soft-SAFT binary interaction parameter ξ_{ij} = 0.915.

Identical performance of the soft-SAFT is obtained for polymers with molecular weight of 1500 and 4000, as shown in the results presented in the additional information in appendix C. A binary interaction parameter was required to describe the experimental data. The correction of this binary interaction parameter, ξ_{ij}, decreases in magnitude from PEG 200 with a value of 0.870 to the PEG 8000 with a value of 0.915. This decrease in the correction with increasing molecular weight seems to indicate that the energetic cross interactions decrease with the molecular weight of the polymer.

The solubility of the gaseous nitrogen in poly(ethylene glycol) is very challenging to model with soft-SAFT, in agreement with what was found previously in Chapter III.4.2 for

the vapor-liquid equilibria of nitrogen in ethylene glycol. This is a common problem with the nitrogen systems resulting from the large asymmetry in the enthalpic and entropic interactions displayed by these systems. The soft-SAFT description of the solubility of nitrogen in poly(ethylene glycol)s of molecular weights of 1500, 4000 and 8000 g/mol at 353.15 K is reported in Figure III.4.15. The experimental data used were taken from Wiesmet et al. (2000). In order to obtain an accurate correlation of the experimental data, the same binary interaction parameter was used for all molecular weights, since on this molecular weight values the phase equilibria are not significantly affected by the polymer molecular weight. However, this value is not the same one used for the nitrogen/ethylene glycol binary mixture changing from 0.5188 for ethylene glycol to 0.6600 to the poly(ethylene glycol) of 1500, 4000 and 8000 g/mol, in a similar manner as it was obtained for other gases. A systematic underprediction of the gas-liquid coexistence phase line for high polymer concentrations is observed.

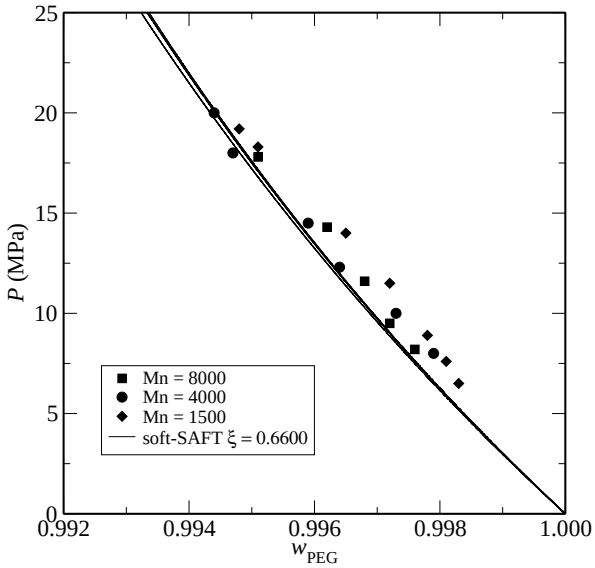

Figure III.4.15: Modeling of the solubility of nitrogen in poly(ethylene glycol) with soft-SAFT. The molecular weights used range from 1500 to 8000 g/mol. The experimental data was taken from Wiesmet et al. (2000).

In Figure III.4.16, the soft-SAFT description of the vapor-liquid equilibria of benzene and poly(ethylene glycol) (Booth and Devoy, 1971) with a molecular weight of 5700 g/mol at 318.95 K and 343.15 K is shown. A small binary interaction parameter (ξ_{ij}=1.020) is

used to accurately describe the phase behavior at both temperatures. The SAFT EoS is able to capture the dependency of the mixture activity with the temperature very accurately.

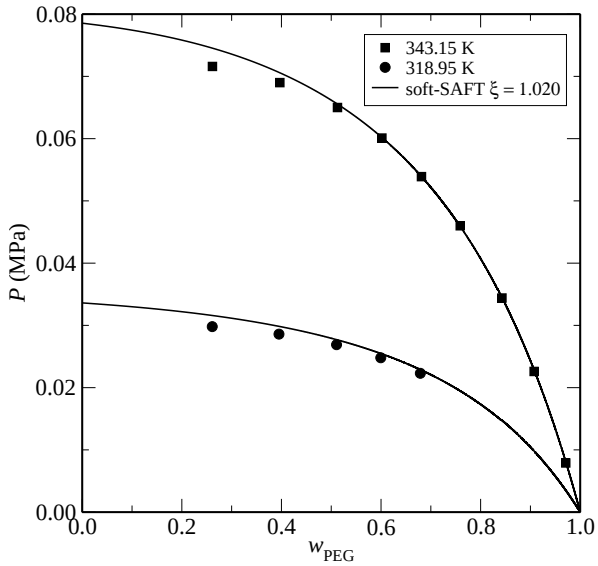

Figure III.4.16: Vapor-liquid equilibria of the mixture poly(ethylene glycol) / benzene modeled by the soft-SAFT EoS. The experimental data is from Booth and Devoy (1971).

The previous examples dealt with gases/vapors which do not have association interactions with PEG. The interactions present in those mixtures only involve association between polymer chains. Mixtures of poly(ethylene glycol) and alkanols present a more complex web of interactions, since both the polymer and the alkanol molecules associate among themselves and also with the other component of the mixture, meaning that self and crossed association are present. This kind of association can be modeled within the SAFT-type EoSs using an analytical or a numerical approach. We have decided not to use the analytical form of the association term as it would result in a system of nonlinear equations for each case of the association behavior needed. Instead the numerical approach developed by Tan, et al. (2004) was used to calculate the fraction of non-bonded molecules, and hence the number of molecules in an associated state. In their work, an algorithm was developed to solve the problem of deriving a specific expression for the fraction of non-bonded molecules for each association model, making it a general procedure. At the same time the derivatives of the Helmholtz residual energy of association can be calculated, in order to obtain the remainder of thermodynamic properties. The

implementation and use of this generalized procedure for the calculation of the fraction of non-bonded molecules within the soft-SAFT context is slightly more time consuming than when the analytical expression is used. However, it is very rewarding in terms of calculation procedure to have a flexible algorithm that can be applied to a vast number of cases without having to derive the specific expressions for each case. The results of using this approach together with the above mentioned association scheme to model the vapor-liquid equilibria of mixtures of poly(ethylene glycol) and different alkanols are presented in Figures III.4.17 and III.4.18. The alkanols studied were methanol and ethanol from Kim et al. (1999) and 2-propanol from Zafarani-Moattar and Yeganeh (2002). The molecular weights of the polymers were of 600 g/mol for the mixtures of ethanol and methanol and 200, 300 and 1000 g/mol for the mixture of 2-propanol. Figure III.4.17 shows the results obtained with the soft-SAFT EoS at 303.15 K. A larger correction of the mixture is needed for the methanol (ξ_{ij}=1.140) than for ethanol (ξ_{ij}=1.040) since the hydrogen bonding is more important on this small molecule than in ethanol. The solubility of 2-propanol in poly(ethylene glycol) of 3 different molecular weights, 200, 300 and 1000 g/mol, at 298.15 K, is presented in Figure III.4.18. The soft-SAFT is able to capture the change of the vapor-liquid behavior with molecular weight of the polymer. In this case, only one small binary interaction parameter (ξ_{ij}=1.045) is required to accurately model all polymer molecular weights, which is very similar to the one used in the case of ethanol.

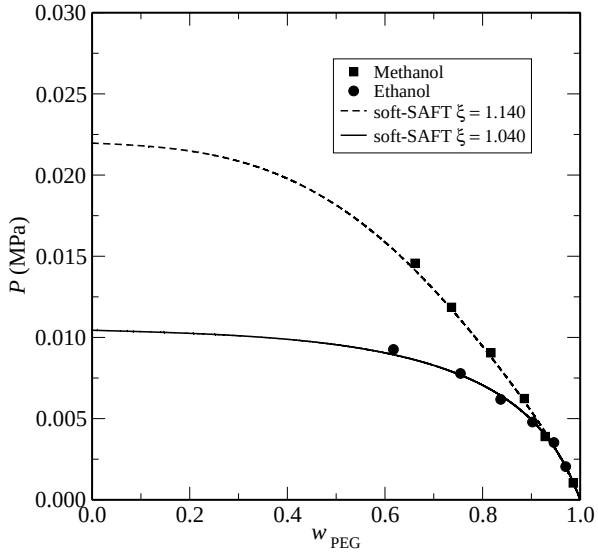

Figure III.4.17:Modeling of the vapor-liquid equilibria of for the mixtures poly(ethylene glycol)/ethanol and poly(ethylene glycol)/methanol at 303.15 K. The molecular weight of the poly(ethylene glycol) is 600 g/mol in both cases. The experimental data is from Kim et al (1999).

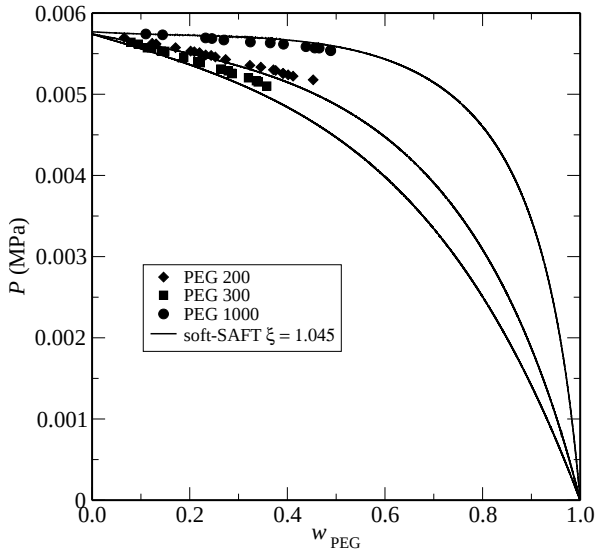

Figure III.4.18: Vapor-liquid equilibria of the mixture poly(ethylene glycol) / 2-propanol at 298.15 K modeled with the soft-SAFT EoS. The experimental data is from Zafarani-Moattar and Yeganeh (2002).

Figure III.4.19 shows the description of the vapor-liquid equilibria for the system poly(ethylene glycol) / water for two polymer molecular weights, 200 and 6000 g/mol, in a temperature range between 298.1 and 333.1 K. The experimental data of this mixture was taken from literature (Herskowitz and Gottlieb, 1985). Like the alkanols, water has the

ability to form association bonds with the polymer's hydroxyl groups in the chain ends. Again, a single molecular weight dependent binary interaction parameter is required: for PEG 200 ξ_{ij}=1.120 was used, while for PEG 6000 ξ_{ij}=1.165 was considered. These values are similar to those used for methanol and they are related to the intensity of the interaction that takes place between the polymer and the solvent.

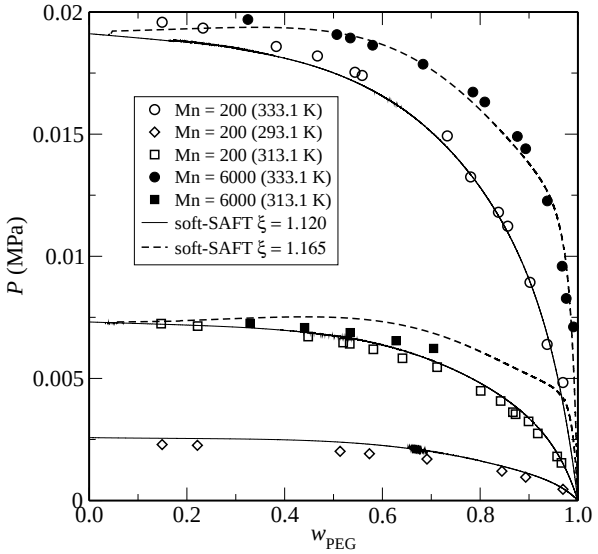

Figure III.4.19: Modeling of the vapor liquid equilibria of the mixture poly(ethylene glycol) / water with the soft-SAFT EoS. The molecular weight of the polymers modeled is 200 and 6000 g/mol. Experimental data from Herskowltz and Gottlleb (1985).

The vapor-liquid equilibria of the PEG /water system has been dealt with in Chapter II using GE based models. In Table III.4.5 the values of the Average Absolute Deviation as obtained by the GE models and soft-SAFT are compared. The binary interaction parameters used in the soft-SAFT EoS are the ones used in Figure III.4.19 for each molecular weight considered. It can be observed that the predictive UNIFAC-FV model is the one that provides the largest deviations from the experimental data. The soft-SAFT model with one binary adjustable parameter produces fairly good results, while the other models that use two binary adjustable parameters show smaller deviations. From Figure III.4.19 it can seen that deviations come essentially from the underprediction of the water vapor pressure.

Table III.4.5: Average absolute deviations (%) obtained with GE models and soft-SAFT for the mixture PEG/water. The a_{12} and a_{21} are from Table II.3.6.

Mn_{PEG}	NRF	Wu-NRTL	sUNIQUAC	UNIFAC-FV	soft-SAFT
200	2.115	1.993	1.610	35.0	4.54
6000	1.500	0.586	0.738	14.4	7.20
a_{12}	0.148	-1.057	-0.990	-	-
a_{21}	-0.034	2.054	2.003	-	-

III.4.3.2.2. Liquid-liquid equilibria

The experimental data of the mixture of poly(ethylene glycol) and toluene, ethylbenzene and n-propylbenezene from Sabadini (1993) was modeled with the soft-SAFT EoS. These systems present a liquid-liquid phase diagram with UCST. The molecular weight of the polymer used range from 200 g/mol to 600 g/mol and the pressure at which these systems were measured was 0.1 MPa. Figure III.4.20a shows the model description of the PEG/toluene mixture for the PEG 200. The agreement with the experimental data is very good when a binary interaction parameter ξ_{ij} = 0.9779 is used. The modeling of the system PEG/ethylbenezene is depicted in Figure III.4.20b, where polymer molecular weights of 200, 300 and 400 g/mol were considered. Again the model can describe the system behavior accurately when using a molecular weight dependent binary interaction parameter, which becomes closer to 1 with molecular weight, as seen previously in this work for systems like PEG/propane. The soft-SAFT description of the system PEG/n-propylbenzene was a harder task to perform, especially for the polymer with highest molecular weight as it is show in Figure III.4.20c. The molecular weight of the polymer used ranged from 200 to 600 g/mol. In the latter, even with the use of a binary interaction parameter the model was not able to correctly describe the shift of the phase diagram with the increase in molecular weight, overpredicting the composition of the mixture critical point.

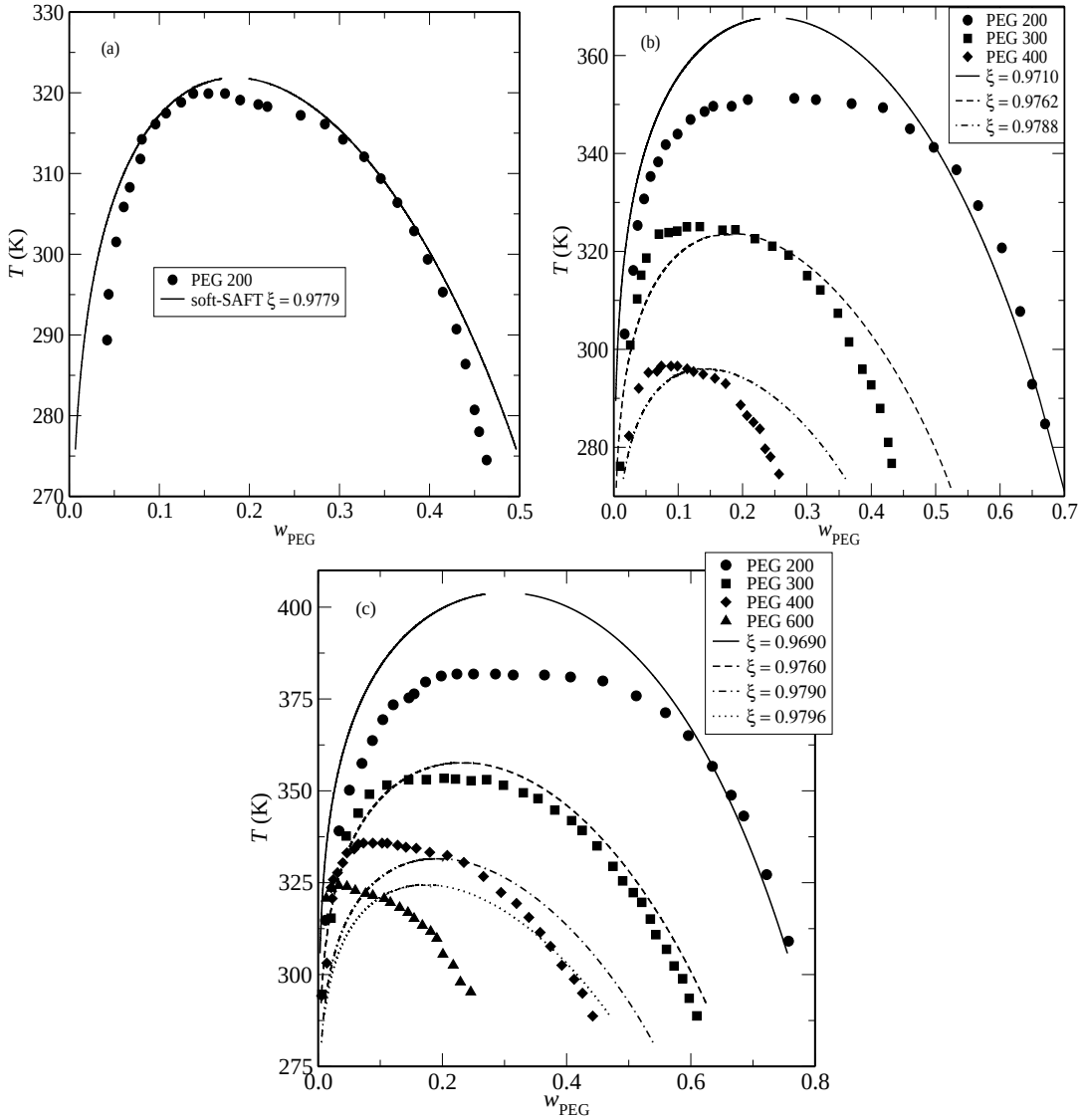

Figure III.4.20: Description of the liquid-liquid equilibria of the mixtures PEG/toluene (a), PEG / ethylbenzene (b) and PEG / n-propylbenzene (c) with the soft-SAFT EoS. Experimental data is from Sabadini (1993).

Finally, Figure III.4.21 shows the soft-SAFT description of the liquid-liquid phase equilibria of the mixture poly(ethylene glycol) / tert-butyl acetate at 0.1MPa. The experimental data of Saeki, et al (1976) indicates that the liquid-liquid equilibria phase diagram for this system presents both a LCST and a UCST for low polymer molecular weights (8000, 14400 and 21200 g/mol) and changes to an hourglass shape phase diagram for the highest polymer molecular weight considered (719000). No association was considered to exist between the solvent (tert-butyl acetate) and the polymer. As shown in

Figure III.4.21, the soft-SAFT EoS can predict reasonably well the LCST of the tert-butyl acetate with poly(ethylene glycol) 8000-21200 g/mol mixtures and its change with molecular weight. One of the shortcomings of the soft-SAFT model is here apparent. Due to a limitation of the temperature and density range of the Lennard-Jones reference term derived from Johnson et al (1993), fitted to simulation data, the soft-SAFT EoS, using this reference equation, is not able to model the UCST. This matter was already addressed for polystyrene (PS) mixtures in Chapter III.3. In the PS case the Lennard Jones reference fluid EoS of Kolafa and Nezbeda (1994) was used, instead of the one from Johnson et al. (1993). However, in the present case it also failed to predict the UCST. Regarding the PEG 719000 g/mol mixtures, the model also fails to describe the hourglass shape.

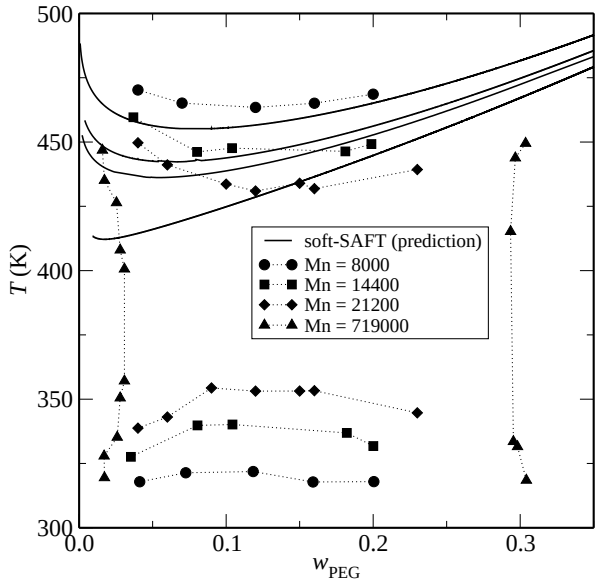

Figure III.4.21: Prediction of liquid-liquid equilibria of the mixture poly(ethylene glycol) / tert-butyl acetate with the soft-SAFT EoS. Experimental data from Saeki, et al (1976).

III.4.3.3. Conclusions

The soft-SAFT EoS was used in this work to model the phase equilibria of poly(ethylene glycol) mixtures with different solvents. The main characteristic of this polymer is the existence of association sites, which in this case were considered to be the

hydroxyl end groups, where polymer and/or solvent molecules can form hydrogen bonds. This behavior was modeled using the TPT1 term of Wertheim within the SAFT approach.

The solubility of gases such as nitrogen, carbon dioxide and propane in poly(ethylene glycol) was successfully described by the soft-SAFT model, using a single binary interaction parameter in all cases. The vapor-liquid equilibria of the mixtures PEG/benzene, PEG/methanol, PEG/ethanol and PEG/2-propanol were also described with the soft-SAFT EoS. A binary interaction parameter was used for all mixtures. It should be noticed that this parameter has a value which is inferior to unity for non hydrogen bonding solvents and a value slightly higher than unity when modeling the *n*-alkanols and water. This indicates that nonassociating molecules such as the studied gaseous or aromatic compounds have a different impact on the phase equilibria description by the soft-EoS compared to associating liquid compounds such as water and *n*-alkanols at the conditions studied.

The liquid-liquid phase equilibria description of the mixtures poly(ethylene glycol) / toluene, poly(ethylene glycol) / ethylbenzene and poly(ethylene glycol) / *n*-butylbenzene by the soft-SAFT EoS was successfully accomplished using a binary interaction parameter close to unity.

The modeling of the liquid-liquid equilibria of the mixture poly(ethylene glycol)/tert-butyl acetate was accomplished for the LCST of the phase diagram. Limitations of the reference equation of state used in soft-SAFT prevented the correct modeling of the UCST of this mixture.

III.4.4. Poly(ethylene glycol) / water system

III.4.4.1. Introduction

In the previous section, the association scheme used for poly(ethylene glycol) was such that only the hydroxyl groups in the chain ends are allowed to form hydrogen bonds. The adoption of this association scheme, enabled the establishment of a correlation of the soft-

SAFT molecular parameters for the ethylene glycol series, since the same assumption was also made for the ethylene glycol oligomers. This procedure provided good results for the vapor-liquid equilibria of several systems involving poly(ethylene glycol), with gases/vapors, such as, carbon dioxide, propane, nitrogen and also methanol, ethanol, 2-propanol and water. In the case of the liquid-liquid equilibria, the systems studied were also well described by the soft-SAFT EoS, particularly for the aromatics mixtures. The results obtained prove that, in fact, the ether oxygen atoms present in the polymer chain have small influence in the phase behavior of the poly(ethylene glycol) mixtures.

Despite the good results obtained for the studied poly(ethylene glycol) mixtures, there is a particular system that deserves a special attention: the poly(ethylene glycol) / water system. The thermophysical behavior of this system is such that it has been classified as very puzzling system (Faraone et al., 1999). This particular system has been studied by a number of techniques, such as IR (Faraone et al., 1999, Begum et al., 1998 and Rozenberg et al., 1998) and NMR (Faraone et al., 1999, Branca et al., 1999 and Hoffmann et al., 2005). The studies made, coupled with molecular simulation results (Tasaki, 1996), showed that the structure of the polymer changes significantly when the solvent changes from an organic solvent to water. In fact, in the presence of water, PEG arranges itself as a double helix, stabilized by water molecules that form hydrogen bonds with the ether groups of the chain backbone of the polymer. The liquid-liquid phase splitting observed for this system can be assumed to be largely driven by the fact that the mentioned interactions actually exist, meaning that the systems behaves differently according to the solvent used.

III.4.4.2. Methodology

In this section, a new approach for the modeling the liquid-liquid phase equilibria of the PEG / water system will be made using both soft-SAFT and the PC-SAFT EoS's. Taking into account the experimental evidences and the simulation results described in the previous sub-section for this system, the assumption that only the hydroxyl groups present in the chain ends play a role in the association behavior of the polymer is no longer valid

and thus the correlation of molecular parameters from the ethylene glycol series cannot be used. Instead, the polymer parameters were determined using binary mixture data.

In order to model poly(ethylene glycol) / water using SAFT, a molecular model has to be defined. In the present case, since there is evidence of association between the ether groups of the polymer chain and water, each oxygen of the ether groups was pinpointed as an association site. The molecular parameters of the polymer using this association scheme were then fitted to experimental data.

III.4.4.3. Preliminary results and discussion

The experimental data used to fit the molecular parameters is from Bae et al., (1991) and Saeki et al., (1976). Both these data sets refer to PEG with molecular weight of 8000 g/mol. These parameters were then used to describe PEG /water systems where the molecular weight of the polymer ranged from 2180 g/mol up to 8000 g/mol. In this range of polymer molecular weights, a closed loop phase diagram is observed for the liquid-liquid phase equilibria. In Table III.4.6, the fitted molecular parameters are shown for both soft-SAFT and PC-SAFT and they were fitted to the liquid-liquid equilibria data for the polymer with molecular weight of 8000 g/mol. Also in Table III.4.6 the values of the molecular parameters found by using the ethylene glycol series correlation are shown for comparison. It is clear the difference in the magnitude of both sets of parameters for the soft-SAFT, in particular the energy parameter, ε, and the association parameters, ε_{HB} and k_{HB}. This fact shows the specificity of the energetic interactions of the poly(ethylene glycol) /water system.

Table III.4.6: Fitted poly(ethylene glycol) and water molecular parameters for soft-SAFT and PC-SAFT

EoS PEG 8000	m	σ (Å)	ε/k_B (K)	ε_{HB}/k_B (K)	k_{HB} (Å^3)	N_{sites}^{ether}	ξ_{ij}
soft-SAFT	95.69	4.4	105.3	984	905	180	0.605
Soft-SAFT (EG Correlation)	136.7	4.29	356.32	4384	4195	-	-
PC-SAFT	202.6	4.35	170.0	1300	0.020[1]	180	0.700

In this work, a refitting of the association water parameters for both equations was made, since its density as described by the original soft-SAFT (Blas, 1999) and PC-SAFT (Gross and Sadowski, 2002a) was not accurate enough in the region of temperatures where PEG / water closed loop phase equilibria diagrams are observed. The new water parameters found are displayed in Table III.4.7 along with the ones previously reported.

Table III.4.7: Water parameters for soft-SAFT and PC-SAFT Equations of State

EoS	m	σ (Å)	ε/k$_B$ (K)	ε$_{HB}$/k$_B$ (K)	k_{HB} (Å^3)	Ref
soft-SAFT	1.000	3.190	408.54	2300	2100	this work
soft-SAFT	1.000	3.190	408.54	2367	2707	Blas, 1999
PC-SAFT	1.065	3.001	366.51	2500	0.035[2]	this work
PC-SAFT	1.065	3.001	366.51	2300	0.032[3]	Gross and Sadowski, 2002a

As it can be seen the difference in the parameters for both EoS is not large. However, this small difference enables the description of the phase equilibria, which is shifted to higher temperatures if these new parameters are not used.

The description of the liquid-liquid phase equilibria of the PEG / water systems is shown in Figure III.4.22. As it was done for poly(styrene), the *m* parameter is transferable to other molecular weights. In this particular case, the number of ether association sites is also transferable to other molecular weights. Note that for both soft-SAFT and PC-SAFT, the binary interaction parameter, ξ_{ij}, was also fitted to the molecular weight. If the parameters from the ethylene glycol correlation were used, the description of the phase diagram was not possible.

1 Reduced value

2 Reduced value

3 Reduced value

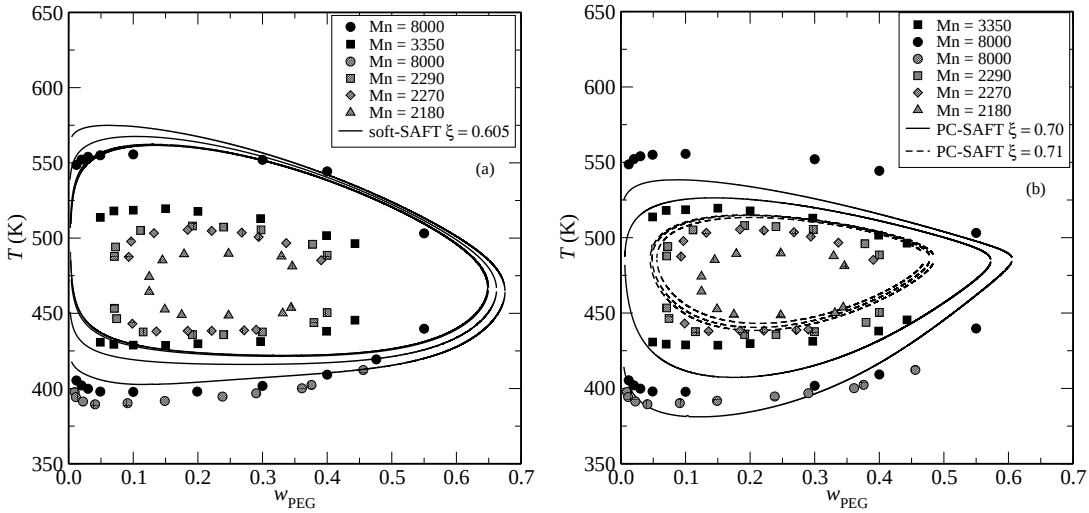

Figure III.4.22: Liquid-liquid phase equilibria of the mixture poly(ethylene glycol) / water described by soft-SAFT (a) and PC-SAFT (b). Experimental data from Bae et al., (1991) (dark symbols) and Saeki et al., (1976) (gray symbols)

The description of the closed loop behavior obtained from both equations of state is quite different. However, both equations seem to have limitations in the description of the phase behavior with molecular weight, particularly the UCST line. This leads to the conclusion that in terms of equation's molecular parameters, it is not only the chain length parameter, *m*, and the number of associating sites that influence the liquid-liquid phase equilibria description of this system. The trend of the other parameters was assessed by fitting them to binary data for each molecular weight. Table III.4.8 shows the fitted parameters for each molecular weight considered.

Table III.4.8: Molecular parameters for the soft-SAFT and PC-SAFT fitted to each molecular weight of PEG.

EoS	Mn	m	σ (Å)	ε/k_B (K)	ε_{HB}/k_B (K)	k_{HB} (Å^3)	N_{sites}^{ether}	ξ_{ij}
soft-SAFT								
	2180	40.1	4.70	70.32	984	905	35	0.800
	2270	42.7	4.70	70.32	984	905	36	0.780
	2280	43.1	4.70	70.32	984	905	36	0.770
	3350	63.0	4.70	70.32	984	905	53	0.76
PC-SAFT								
	2180	55.2	4.30	170.0	1300	0.020	49	0.734
	2270	58.5	4.30	174.5	1300	0.020	51	0.734
	2290	59.8	4.30	176.5	1300	0.020	51	0.735
	3350	89.84	4.35	183.0	1300	0.020	75	0.74

As shown in Table III.4.8 the association parameters were kept constant for all molecular weights, and all the others were fitted. It can be observed that the change in the molecular parameters was more significant for soft-SAFT than for PC-SAFT, in particular the energy parameter, ε. Despite the observed change in the parameters, PC-SAFT performs better for the lower molecular weights of poly(ethylene glycol), as Figure III.4.23 clearly shows. The description of the UCST line is difficult when using the soft-SAFT.

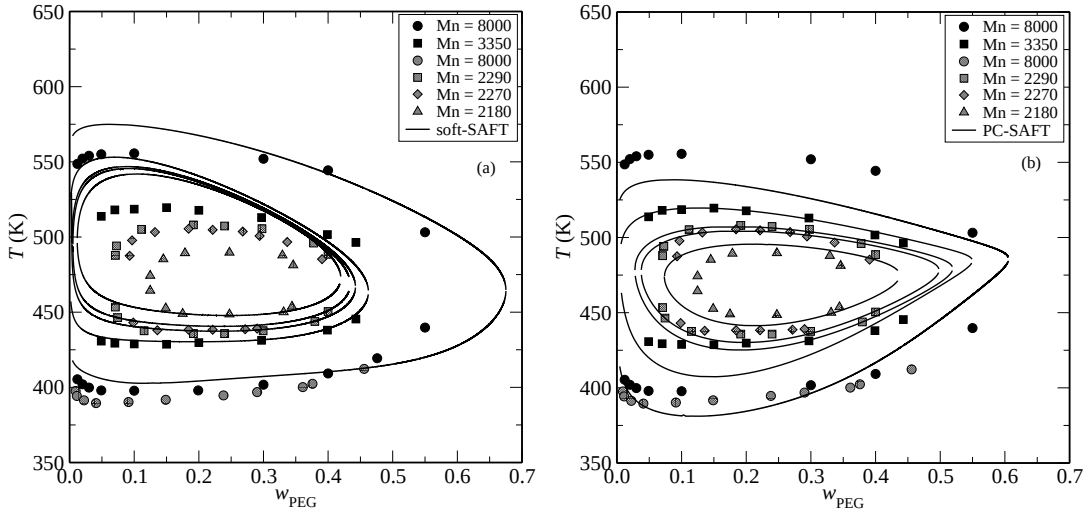

Figure III.4.23: Liquid-liquid phase equilibria of the poly(ethylene glycol) /water system description as described by soft-SAFT and PC-SAFT with fitted molecular parameters for each molecular weight. Experimental data from Bae et al. (1991) (dark symbols) and Saeki et al. (1976) (gray symbols)

Note that the association term in the SAFT approach used considers that all association sites are equivalent. That is to say that the association strength of the oxygen sites in the hydroxyl group is the same as the oxygen sites' in the ether groups. Physically this is not true and the poor extrapolation to lower molecular weights shown by the equations can be a proof of that. The molecular parameters fitted to a molecular weight of 8000 g/mol, where the chain end hydroxyl group effect is small, cannot describe the phase equilibria for lower molecular weights, where the end effects is considerably larger.

III.4.4.4. Conclusions

In this section some preliminary results are shown for the modeling of the liquid-liquid phase equilibria of the poly(ethylene glycol) / water system by the SAFT equation of state. This system exhibits a closed loop liquid-liquid phase diagram which was fairly well described by SAFT when using parameters fitted to one set of binary mixture data with a specific polymer molecular weight. Since these fitted parameters were unable to describe the change in the phase diagram with molecular weight of the polymer, new polymer molecular parameters were fitted to each polymer molecular weight binary phase equilibria

data. Small improvements were observed, in particular for the soft-SAFT EoS. However, these preliminary results could still be improved with a better fitting algorithm.

IV. CONCLUSIONS

IV.1. Conclusions

This work is a step forward on systematically developing sound molecular models for the description of polymer systems. The study of the phase equilibria of systems involving polymers was made. The description of these systems was done using both GE models and Equations of State, namely the Statistical Associating Fluid Theory.

On the first approach, a throughout comparison of the performance of the models of Excess Gibbs energy (GE) was made using a large database of vapor-liquid equilibria data of polymer mixtures. On this study, the used models were included residual part and combinatorial part, accounting for energy and volume interactions, respectively. The models used included NRTL, Flory-Huggins, UNIQUAC, sUNIQUAC and UNIFAC-FV. It became clear that, in the context of GE models, treating the polymers as segments has an advantage in term of predicting the phase equilibria behavior of other polymers, for which the model was not fitted.

A more in depth study was made of phase equilibria of polymer systems using the SAFT EoS. The SAFT equation, in particular the soft-SAFT version has proven to be a

model where the molecular level of description of the compounds is a very good asset. This is shown in the physical meaning of the molecular parameters for each compound. This is not related directly to the actual value of the parameters, but to the fact that once the parameters of the polymer are found, they can be used for different mixtures and across the whole range of molecular weights of the polymers. The polymer systems studied included the following polymers: polyethylene, polystyrene and poly(ethylene glycol). The soft-SAFT EoS performed very well for the polyethylene systems.

To find polyethylene molecular parameters, a correlation of parameters made from the ones n-alkane series was sufficient to model the behavior of binary mixtures of polyethylene with other solvents. The phase equilibria studied involved vapor-liquid, liquid-liquid and gas-liquid equilibria of the binary mixtures. Particularly, in the case of liquid-liquid equilibria, one of the mixtures presented a phase diagram in which both LCST and UCST were present. The soft-SAFT model correctly described the behavior of this system by having predicted the existence of both critical solution temperatures. The parameters could be applied to any linear polyethylene.

The polystyrene polymer had a different treatment when finding the molecular parameters. As the series of oligomers for polystyrene dos not exist, a different approach of that for polyethylene had to be followed. Two methods of finding the molecular parameter were analyzed. In the method of choice, the polymer's parameters were found by fitting them to binary mixture data. This involved fitting the parameters for the polymer along with the binary interactions parameter. The results when using this approach are quite satisfactory. The phase equilibria modeled by the soft-SAFT, as it was the case of polyethylene, included vapor-liquid, liquid-liquid and gas-liquid equilibria of binary mixtures. In the studied systems involving polystyrene the existence of both LCST and UCST as correctly modeled by the soft-SAFT EoS.

Poly(ethylene glycol) systems were studied with the soft-SAFT EoS. The main characteristic of this polymer is that it can associate through the hydroxyl groups present in the ends of the polymer chain. This behavior was included in the SAFT modeling formalism. To find the molecular parameters of the polymer, the approach followed for polyethylene was also used. For this, the study of the ethylene glycol oligomers was

carried out. The molecular parameters of the oligomers from ethylene glycol up to tetraethylene glycol. The performance of the found parameters was assessed by successfully modeling the phase equilibria of some mixtures with several solvents. Similarly to the approach used in the polyethylene case, a correlation of parameters was made with the oligomer's parameters. The correlation of parameters was then used to describe the phase equilibria of systems involving poly(ethylene glycol). The soft-SAFT EoS could model successfully the solubility of gases (nitrogen, propane and carbon dioxide) in poly(ethylene glycol) and the vapor liquid equilibria of the mixtures of poly(ethylene glycol) with ethanol, 2-propanol and water. The liquid-liquid equilibria of the systems poly(ethylene glycol) / toluene, ethylbenzene and n-propylbenzene. However, some difficulties were found when modeling the system poly(ethylene glycol) / tert-butyl acetate which presented a hourglass phase diagram for higher molecular weight of the polymer. The liquid-liquid phase equilibria of the poly(ethylene glycol) /water system was also modeled with soft-SAFT by fitting the molecular parameters of the polymer to a binary mixture. The description of the closed loop phase equilibria diagram by soft-SAFT fairly good for high molecular weight polymers.

As final conclusion, a molecular model in the SAFT Equation of State approach was established. Particularly in the soft-SAFT EoS case, it was found to be very well suited to model the phase equilibria of aliphatic polymers (polyethylene), aromatic polymers (polystyrene) and associating polymers (poly(ethylene glycol)). Results presented here act in favor of using molecular-based equations of state, such as the ones used here, to accurately describe the phase equilibria of polymer and other complex systems. A key for the success of this type of equations lays on the fact that they include the chain architecture from the inception of the equation.

IV.2. Future work

The work developed in the the field of the phase equilibria of polymer systems is an ever growing challenge. Apart from phase equilibria, other thermodynamic properties of polymer systems could be explored in the future using the SAFT equations of state. The future developments in the filed of SAFT description of thermodynamic behavior of polymers systems follows:

- Description of interfacial properties of polymers mixtures by using the Density Functional Theory along with the SAFT EoS.
- Model multicomponent mixtures in order to mimic in a more accurate way the real conditions that can be found in a polymerization plant.
- Modeling of second order properties of pure polymer and polymer mixtures, such as specific heats at constant pressure and volume or the speed of sound.
- Add an extra term in the SAFT equation of state the can model the specific interactions present in molecules which have dipolar moment, such as ketones, water or esters.
- The electrolyte interactions are very important, and in the case of polymers this can be useful to model thermodynamic behavior of polyelectrolytes, or the much more useful ternary mixtures poly(ethylene glycol) / water / electrolyte (salt). So an additional term in the SAFT EoS accounting for electrolyte integrations would be very interesting.

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APPENDIX A

According to the two-fluid theory a fluid results from the mixture of two hypothetical fluids: fluid 1 that has a molecule of type 1 surrounded by molecules of type 2 and fluid 2 that has a molecule of type 2 surrounded by molecules of type 1. In the system considered in this work there are no molecules but segments. Following Wu et al (1996), the reference states are pure liquid for the solvent and a hypothetical aggregation state for the polymer segments.

Thus the excess free energy for this system is given by:

$$u^E = \frac{Z}{2} N_q \left(X_1 X_{21} (U_{21} - U_{11}) + X_2 X_{12} (U_{12} - U_{22}) \right) \tag{A.1}$$

By the local composition theory the local composition of each component can be related to the global composition:

$$\frac{X_{ji}}{X_{ii}} = \frac{X_j}{X_i} e^{\frac{-Z}{2}\frac{U_{ji} - U_{ii}}{kT}} \tag{A.2}$$

Substituting Eq. (A2) in (A1) and arranging the final expression for the free energy becomes:

$$u^E = \frac{X_1 X_2 e^{\frac{-\Delta u_{21}}{T}} \Delta u_{21}}{X_1 + X_2 e^{\frac{-\Delta u_{21}}{T}}} + \frac{X_2 X_1 e^{\frac{-\Delta u_{12}}{T}} \Delta u_{12}}{X_2 + X_1 e^{\frac{-\Delta u_{12}}{T}}} \tag{A.3}$$

In which:

$$\Delta u_{ij} = \frac{Z}{2} \frac{\left(U_{ij} - U_{jj} \right)}{k N_q} \tag{A.4}$$

To obtain the expression for the Helmholtz free energy the following relation is used:

$$\frac{d\left(a^E / T \right)}{d\left(1/T \right)} = u^E \tag{A.5}$$

Integrating Eq. (A5):

$$\frac{a^E}{T} = \int_{1/T_0}^{1/T} u^E d(1/T) + C \tag{A.6}$$

The integration is made by letting $1/T_o \rightarrow 0$. The constant of integration in Eq. (A6) is the combinatorial term resulting from integration. But in this work the concern is on the residual term so the integration is made yielding:

$$\left[\frac{a^E}{N_q kT}\right]_{residual} = -X_1 \ln\left(X_1 + X_2 e^{-\frac{\Delta u_{21}}{T}}\right) - X_2 \ln\left(X_1 + X_2 e^{-\frac{\Delta u_{21}}{T}}\right) \tag{A.7}$$

At the low pressures $(a^E)_{T,V} \approx (g^E)_{T,P}$ so by the definition of activity coefficient:

$$\frac{\partial \frac{G^E}{RT}}{\partial N_1} = \ln \gamma_1 = X_2 q_1 \left(\frac{\tau_{21}}{X_1 + X_2 \tau_{21}} - \frac{\tau_{12}}{X_2 + X_1 \tau_{12}}\right) \tag{A.8}$$

with

$$G^E = \frac{N_q}{N_A} g^E N_A \tag{A.9}$$

with X_i and τ_{ij} being defined by Eqs. (II.2.13) and (II.2.17) respectively.

APPENDIX B

In this Appendix the mathematical description of the Statistical Associating Fluid Theory will be made. Both versions of the SAFT EoS studied throughout the the thesis, PC-SAFT and soft-SAFT will be described. At this point it will be possible to assess the key differences between both equations of state. The mathematical description of the soft-SAFT EoS has been done by Pamiès (2003), but a simplified form is presented here am compared to PC-SAFT.

Whenever the SAFT EoS is used, its dimensionless form is used. In order to use the dimensionless form of all thermodynamic variables (e.g. T, P, ρ), a reference component has to be chosen. In all expressions in this appendix the subscript *R* is referring to the reference component.

B.1. Ideal Term

The ideal term is the same for both EoS's. The Helmholtz free energy of a pure ideal fluid is defined by:

$$A^{ideal} = RT\left(\ln\rho + \ln\Lambda_i^3 - 1\right) \tag{B.1}$$

where Λ_i is the de Broglie wavelength. This equation can be simplified considering that the reference state is irrelevant and that no derivatives of the temperature will be needed. Accordingly and extending it for mixtures where the contribution of each component is weighted by its composition:

$$A^{ideal} = \sum_i x_i RT\left(\ln\rho - 1\right) \tag{B.2}$$

Resulting in the equation of ideal gases. The pressure and chemical potential can be derived from the previous equation.

$$P^{ideal} = -\left(\frac{\partial A^{ideal}}{\partial V}\right)_{T,x_k} = \rho^2\left(\frac{\partial A^{ideal}}{\partial \rho}\right)_{T,x_k} = R\rho T \tag{B.3}$$

which is the ideal gas equation of state.

$$\mu_i^{ideal} = \left(\frac{\partial A^{ideal}}{\partial x_i}\right)_{T,\rho,x_{k\neq i}} = RT\ln(\rho x_i) \tag{B.4}$$

B.2 Reference term

What makes the distinction between the soft-SAFT and the PC-SAFT versions of the studied equation of state is the reference term. The temperature dependent parameters (a_p, b_p and G_p) of the modified Benedit-Webb-Rubbin that defines the Lennard Jones EoS were fitted to simulation data by Johnson et al., (2003).

In the soft-SAFT EoS context, the equations for the Helmholtz energy, pressure and chemical potential are the following:

$$A^{ref} = R\varepsilon\left(\sum_{p=1}^{8}\frac{a_p}{p}(\rho_c^{rf})^p + \sum_{p=1}^{6} b_p G_p\right) \tag{B.5}$$

where

$$\rho_c^{rf} = m\rho^{rf} = m\rho\sigma^3 \tag{B.6}$$

defines the density of Lennard Jones cores.

The pressure and Chemical potential are given by:

$$P^{ref} = R\frac{\epsilon}{m\sigma^3}\left(\sum_{p=1}^{8} a_p(\rho_c^{rf})^{p+1} + F\sum_{p=1}^{6} b_p(\rho_c^{rf})^{2p+1}\right) \tag{B.7}$$

where

$$F = e^{-\gamma\rho^2} \tag{B.8}$$

being γ a non-linear adjustable parameter.

$$\mu^{ref} = A^{ref} + \frac{P^{ref}}{\rho} \tag{B.9}$$

To denote that the equation of state thus defined already considers the possibility of directly modeling mixtures.

In the case of the PC-SAFT version, developed by Gross and Sadowski, the reference term is decomposed in two subterms: the hard sphere term and a chain dispersion term. The hard sphere term is the same as the one used by Huang and Radoz (1991), derived by Boublik (1970) and Mansoori et al. (1971), for mixtures:

$$A^{hs} = RT\frac{1}{\zeta_0}\left(\frac{\zeta_2^3 + 3\zeta_1\zeta_2\zeta_3 - 3\zeta_1\zeta_2\zeta_3^2}{\zeta_3(1-\zeta_3)^2} - \left(\zeta_0 - \frac{\zeta_2^3}{\zeta_3^2}\right)\log(1-\zeta_3)\right) \tag{B.10}$$

The variables defined by ζ_k are reduced densities and are defined as:

$$\zeta_k = \frac{\pi}{6}\rho\sum_{i=1}^{n} x_i m_i d_i^k \tag{B.11}$$

The temperature dependent diameter, d_i, is given by the following:

$$d_i = \sigma_i\left(1 - 0.12\mathrm{e}^{\epsilon_i/T}\right) \tag{B.12}$$

The expression for the hard sphere pressure is then given by:

$$P^{hs} = R\rho T\left(\frac{\zeta_3}{1-\zeta_3} + \frac{3\zeta_1\zeta_2}{\zeta_0(1-\zeta_3)^2} + \frac{3\zeta_2^3 - \zeta_3\zeta_2^3}{\zeta_0(1-\zeta_3)^3}\right) \tag{B.13}$$

and the residual chemical potential,

$$\mu_i^{hs} = -\frac{\partial\zeta_0}{\partial x_i}\frac{1}{\zeta_0}\frac{A^{hs}}{T} + \frac{1}{\zeta_0}\left(3\zeta_2^2\frac{\frac{\partial\zeta_2}{\partial x_i}}{(\zeta_3(1-\zeta_3)^2)} - \zeta_2^3\frac{\frac{\partial\zeta_3}{\partial x_i}}{(\zeta_3^2(1-\zeta_3)^2)} + 2\zeta_2^3\frac{\frac{\partial\zeta_3}{\partial x_i}}{(\zeta_3(1-\zeta_3)^3)} + 3\frac{\partial\zeta_1}{\partial x_i}\frac{\zeta_2}{(1-\zeta_3)} + 3\zeta_1\frac{\frac{\partial\zeta_2}{\partial x_i}}{(1-\zeta_3)} + 3\zeta_1\zeta_2\frac{\frac{\partial\zeta_3}{\partial x_i}}{(1-\zeta_3)^2} - \left(\frac{\partial\zeta_0}{\partial x_i} - 3\zeta_2^2\frac{\frac{\partial\zeta_2}{\partial x_i}}{\zeta_3^2} + 2\zeta_2^3\frac{\frac{\partial\zeta_3}{\partial x_i}}{\zeta_3^3}\right)\log(1-\zeta_3) + (\zeta_0 - \frac{\zeta_2^3}{\zeta_3^2})\frac{\frac{\partial\zeta_3}{\partial x_i}}{(1-\zeta_3)}\right) \tag{B.14}$$

With the hard sphere defined the dispersion contribution to the residual Helmholtz energy has to be defined in order to account for the attractive interactions. The dispersion Helmholtz energy, in PC-SAFT, is a second order theory derived from the work of Barker and Henderson (1967a and 1967b), which was conceived to model spherical molecules. This theory was extended to chain molecules by Gross and Sadowki (2000). The first and second order of the Helmholtz energy of dispersion are separated in two terms, holding:

$$A^{disp} = A_1 + A_2 \tag{B.15}$$

The contributions with the Simplified integrals *I* are given by:

$$A^{disp} = A_1 + A_2 \tag{B.16}$$

$$A_2 = -\pi \rho \bar{m} C_1 I_2(\eta, \bar{m}) \overline{m^2 \varepsilon^2 \sigma^3} \tag{B.17}$$

where η, the reduced density, is given by ζ_3, and $\bar{m}$ is given by:

$$\bar{m} = \sum_{i=1} x_i m_i \tag{B.18}$$

The variable C_1 is the compressibility and the its expression is:

$$C_1 = \left(1 + \bar{m} \frac{8\eta - 2\eta^2}{(1-\eta)^4} + (1-\bar{m}) \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{\left|(1-\eta)(2-\eta)\right|^2} \right)^{-1} \tag{B.19}$$

In expressions B.16 and B.17, the following abbreviations were introduced:

$$\overline{m^2 \varepsilon \sigma^3} = \sum_i \sum_j x_i x_j m_i m_j \frac{\varepsilon_{ij}}{kT} \sigma_{ij}^3 \tag{B.20}$$

$$\overline{m^2 \varepsilon^2 \sigma^3} = \sum_i \sum_j x_i x_j m_i m_j \left(\frac{\varepsilon_{ij}}{kT} \right)^2 \sigma_{ij}^3 \tag{B.21}$$

The usual combining rules are used.

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \tag{B.22}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \tag{B.23}$$

The integrals of the perturbation theory were simplified as simple power rules:

$$I_1(\eta, \bar{m}) = \sum_{i=0}^{6} a_i(\bar{m}) \eta^i \tag{B.24}$$

$$I_2(\eta, \bar{m}) = \sum_{i=0}^{6} b_i(\bar{m}) \eta^i \tag{B.25}$$

The values of a_i and b_i depend on the chain length:

$$a_i(\bar{m}) = a_{0,i} + \frac{\bar{m}-1}{\bar{m}} a_{1,i} + \frac{\bar{m}-1}{\bar{m}} \frac{\bar{m}-2}{\bar{m}} a_{2,i} \tag{B.26}$$

$$b_i(\bar{m}) = b_{0,i} + \frac{\bar{m}-1}{\bar{m}} b_{1,i} + \frac{\bar{m}-1}{\bar{m}} \frac{\bar{m}-2}{\bar{m}} b_{2,i} \tag{B.27}$$

The model constants $a_{0,i}$, $a_{1,i}$, $a_{2,i}$, $b_{0,i}$, $b_{1,i}$ and $b_{2,i}$ are given in the work of Gross and Sadowski (2001).

Having the model thus defined for the dispersion contribution in terms of Helmholtz energy, the expressions for pressure en chemical potential can be derived.

$$P^{disp} = RT\rho^2\left(-2\pi\overline{m^2\epsilon\sigma^3}\left(I_1+\frac{\partial I_1}{\partial\rho}\right)-\pi\bar{m}\overline{m^2\epsilon^2\sigma^3}\left(C_1 I_2+I_2\frac{\partial C_1}{\partial\rho}+C_1\frac{\partial I_2}{\partial\rho}\right)\right) \tag{B.28}$$

where,

$$\frac{\partial I_1}{\partial\rho}=\frac{1}{\rho}\sum_{i=1}^{6} i\,a_i(\bar{m})\eta^i \tag{B.29}$$

$$\frac{\partial I_2}{\partial\rho}=\frac{1}{\rho}\sum_{i=1}^{6} i\,b_i(\bar{m})\eta^i \tag{B.30}$$

$$\frac{\partial C_1}{\partial\rho}=-C_1^2\left(\bar{m}\frac{-4\eta^3+20\eta^2+8\eta}{(1-\eta)^5}+(1-\bar{m})\frac{2\eta^4+12\eta^3-48\eta^2+40\eta}{\left((1-\eta)(2-\eta)\right)^3}\right) \tag{B.31}$$

and

$$\mu_i^{disp}=-2\pi\rho\left(\frac{\partial I_1}{\partial x_i}\overline{m^2\varepsilon\sigma^3}+I_1\frac{\partial\overline{m^2\varepsilon\sigma^3}}{\partial x_i}\right)-\pi\rho\left(m_i C_1 I_2+\bar{m}\frac{\partial C_1}{\partial x_i}I_2+\bar{m}C_1\frac{\partial I_2}{\partial x_i}\overline{m^2\varepsilon^2\sigma^3}+\bar{m}C_1 I_2\frac{\partial\overline{m^2\varepsilon\sigma^3}}{\partial x_i}\right) \tag{B.32}$$

where,

$$\frac{\partial C_1}{\partial x_i}=-C_1^2\left(m_i\frac{8\zeta_3-2\zeta_3^2}{(1-\zeta_3)^4}-m_i\frac{20\zeta_3-27\zeta_3^2+12\zeta_3^3-2\zeta_3^4}{((1-\zeta_3)(2-\zeta_3))^2}\right)-\frac{\partial\zeta_3}{\partial x_i}C_1^2\left(\bar{m}\frac{-4\zeta_3^2+20\zeta_3+8}{(1-\zeta_3)^5}+(1-\bar{m})\frac{2\zeta_3^3+12\zeta_3^2-48\zeta_3+40}{((1-\zeta_3)(2-\zeta_3))^3}\right) \tag{B.33}$$

$$\frac{\partial I_1}{\partial x_i}=\sum_{j=0}^{6} a_j(\bar{m})\,j\frac{\partial\zeta_3}{\partial x_i}\eta^{j-1}+\frac{\partial a_j(\bar{m})}{\partial x_i} \tag{B.34}$$

$$\frac{\partial I_2}{\partial x_i}=\sum_{j=0}^{6} b_j(\bar{m})\,j\frac{\partial\zeta_3}{\partial x_i}\eta^{j-1}+\frac{\partial b_j(\bar{m})}{\partial x_i} \tag{B.35}$$

$$\frac{\partial a_j(\bar{m})}{\partial x_i}=\frac{m_i}{\bar{m}^2}a_{2,j}+\frac{m_i}{\bar{m}^2}\left(3-\frac{4}{\bar{m}}\right)a_{3,j} \tag{B.36}$$

$$\frac{\partial b_j(\bar{m})}{\partial x_i}=\frac{m_i}{\bar{m}^2}b_{2,j}+\frac{m_i}{\bar{m}^2}\left(3-\frac{4}{\bar{m}}\right)b_{3,j} \tag{B.37}$$

$$\frac{\partial\overline{m^2\varepsilon\sigma^3}}{\partial x_i}=2m_i\sum_j x_j m_j\frac{\varepsilon_{ij}}{kT}\sigma_{ij}^3 \tag{B.38}$$

$$\frac{\partial\overline{m^2\varepsilon^2\sigma^3}}{\partial x_i}=2m_i\sum_j x_j m_j\left(\frac{\varepsilon_{ij}}{kT}\right)^2\sigma_{ij}^3 \tag{B.39}$$

B.3 Chain term

The expression used to account for the formation of chains of segments is the same for both equations of state, soft-SAFT and PC-SAFT:

$$A^{chain} = R\,T \sum_{i}^{n} x_i (1-m_i) \ln g_{ii}(\sigma_{ii}) \tag{B.40}$$

The g_{ii} variable denotes the radial distribution function of the reference fluid, which in the context of soft-SAFT in the Lennard Jones fluid and in the PC-SAFT once it is the hard sphere fluid.

The expressions for the pressure and chemical potential are then given by:

$$P^{chain} = R\,T\,\rho^2 \sum_{i}^{n} x_i \frac{1}{g_{ii}(\sigma_{ii})} \left(\frac{\partial\, g_{ii}(\sigma_{ii})}{\partial \rho} \right)_{T,x_j} \tag{B.41}$$

$$\mu_i^{chain} = R\,T \left[(1-m_i) \ln g_{ii}(\sigma_{ii}) + (1-\bar{m}) \frac{1}{g_{ii}(\sigma_{ii})} \left(\frac{\partial\, g_{ii}(\sigma_{ii})}{\partial\, x_j} \right)_{T,\rho,x_{j\neq i}} \right] \tag{B.42}$$

The Lennard Jones pair correlation function, fitted by Johnson et al. (1994), follows.

$$g_{LJ}(\sigma) = 1 + \sum_{p=1}^{5} \sum_{q=1}^{5} a_{pq} (\rho_c^{rf})^p\, T^{1-q} \tag{B.43}$$

The respective derivatives with respect to density and composition are:

$$\frac{\partial\, g_{LJ}(\sigma)}{\partial \rho} = m\,\sigma^3 \sum_{p=1}^{5} p \sum_{q=1}^{5} a_{pq} (\rho_c^{rf})^{p-1}\, T^{1-q} \tag{B.44}$$

$$\frac{\partial\, g_{LJ}(\sigma)}{\partial\, x_i} = \sum_{p=1}^{5} \sum_{q=1}^{5} a_{pq} (\rho_c^{rf})^p\, T^{1-q} \left[p \frac{m_i}{\bar{m}} + \frac{p}{\sigma^3} \left(\frac{\partial\, \sigma^3}{\partial\, x_i} \right)_{x_{j\neq i}} - \frac{1-q}{\varepsilon\,\sigma^3} \left(\frac{\partial\, \varepsilon\,\sigma^3}{\partial\, x_i} \right)_{x_{j\neq i}} \right] \tag{B.45}$$

where,

$$\sigma^3 = \frac{\sum_i \sum_j x_i x_j m_1 m_j \sigma_{ij}^3}{\left(\sum_i x_i m_i \right)^2} \tag{B.46}$$

$$\varepsilon\sigma^3=\frac{\sum_i\sum_j x_i x_j m_1 m_j \varepsilon_{ij}\sigma_{ij}^3}{\left(\sum_i x_i m_i\right)^2} \tag{B.47}$$

$$\left(\frac{\partial\sigma^3}{\partial x_i}\right)_{x_{j\neq i}}=\frac{m_i}{\bar{m}}\left[\sum_j x_{c_j}\sigma_{ij}^3-\sigma^3\right] \tag{B.48}$$

$$\left(\frac{\partial\varepsilon\sigma^3}{\partial x_i}\right)_{x_{j\neq i}}=\frac{2m_i}{\bar{m}}\left[\sum_j x_{c_j}\varepsilon_{ij}\sigma_{ij}^3-\varepsilon\sigma^3\right] \tag{B.49}$$

The variable, x_c, stands for the composition of core segments and is given by:

$$x_{c_j}=\frac{\sum_j x_j m_j}{\left(\sum_i x_i m_i\right)^2} \tag{B.50}$$

For the PC-SAFT EoS the pair distribution function is the one from hard spheres. For this purpose the work of Boublik (1970) and Mansoori et al. (1971). The expression defining the correlation function is:

$$g_{ij}=\frac{1}{1-\zeta_3}+d_{ij}\frac{3\zeta_2}{(1-\zeta_3)^2}+d_{ij}^2\frac{2\zeta_2^2}{(1-\zeta_3)^3} \tag{B.51}$$

where d_{ij} is defined as:

$$d_{ij}=\frac{d_i d_j}{d_i+d_j} \tag{B.52}$$

The respective derivatives of the pair correlation function with respect to density and composition are given by:

$$\frac{\partial g_{ij}}{\partial\rho}=\frac{\zeta_3}{(1-\zeta_3)^2}+\frac{3d_{ij}\zeta_2}{(1-\zeta_3)^2}+\frac{6d_{ij}\zeta_2\zeta_3}{(1-\zeta_3)^3}+\frac{4d_{ij}^2\zeta_2^2}{(1-\zeta_3)^3}+\frac{6d_{ij}(i,j)^2\zeta_2^2\zeta_3}{(1-\zeta_3)^4} \tag{B.53}$$

$$\frac{\partial g_{ij}}{\partial x_k}=\frac{\partial\zeta_3}{\partial x_k}\frac{1}{(1-\zeta_3)^2}+\frac{\partial\zeta_2}{\partial x_k}\frac{3d_{ij}}{(1-\zeta_3)^2}+\frac{\partial\zeta_3}{\partial x_k}\frac{6d_{ij}\zeta_2}{(1-\zeta_3)^3}+\frac{\partial\zeta_2}{\partial x_k}\frac{4d_{ij}^2\zeta_2}{(1-\zeta_3)^3}+\frac{\partial\zeta_3}{\partial x_k}\frac{6d_{ij}^2\zeta_2^2}{(1-\zeta_3)^4} \tag{B.54}$$

B.4 Association term

As it was the case of the chain term, the associative term is the same for both equation of state, soft-SAFT and PC-SAFT. The expression is given in terms of temperature, number of associating sites in a molecule, M_i, and the number of molecules of component *i* not bound to associating site α, X_i^{α} .

The equation that defines the associating term is

$$A^{assoc} = RT \sum_i x_i \left(\sum_{\alpha} \left(\ln X_i^{\alpha} - \frac{X_i^{\alpha}}{2} \right) + \frac{M_i}{2} \right) \tag{B.55}$$

in which the fraction of nonbonded molecules *i* to site α is defined by:

$$X_i^{\alpha} = \frac{1}{1 + \rho \sum_j x_j \sum_{\beta} X_j^{\beta} \Delta^{\alpha_i \beta_j}} \tag{B.56}$$

The variable $\Delta^{\alpha_i \beta_j}$ is the strength of the association bond. It is defined differently for both equations of state since it depends on the pair correlation function which is also different for both equations, as seen above. For soft-SAFT the strength of association is given by:

$$\Delta^{\alpha_i \beta_j} = 4\pi \left(e^{\frac{\varepsilon_{HB}}{kT}} - 1 \right) k_{HB} I \tag{B.57}$$

where *I* is a function of temperature and it was derived by Müller and Gubbins (1995).

$$I = \frac{1}{38400} \sum_{p=0}^{4} \sum_{q=0}^{4} a_{pq} (\rho_c^{rf})^p T^q \tag{B.58}$$

In the PC-SAFT case the association expression is the one given in Huang and Radosz (1991) work.

$$\Delta^{\alpha_i \beta_j} = \left(e^{\frac{\varepsilon_{HB}}{kT}} - 1 \right) k_{HB} g_{ij}(\sigma_{ij}) \tag{B.59}$$

where the pair correlation function is from Equation B.51.

The expressions for the pressure and chemical of association, obtained by deriving the Helmholtz energy of association with respect to the density and composition, are the following:

$$P^{assoc} = RT\rho^2 \sum_i x_i \sum_\alpha \left(\frac{1}{X_i^\alpha} - \frac{1}{2} \right) \left(\frac{\partial X_i^\alpha}{\partial \rho} \right)_{T, x_j} \tag{B.60}$$

$$\mu_i^{assoc} = RT \left[\sum_\alpha \left(\ln X_i^\alpha - \frac{X_i^\alpha}{2} \right) + \frac{M_i}{2} + \sum_k x_k \sum_\alpha \left(\frac{1}{X_k^\alpha} - \frac{1}{2} \right) \left(\frac{\partial X_k^\alpha}{\partial x_i} \right)_{T, \rho, x_{j \neq i}} \right] \tag{B.61}$$

The derivatives of X_i^α with respect to the density and composition are not easy obtainable since they require, at the same time, derivatives of the same variable. Several approaches can be used to solve this problem. One of the approaches is to make simplifications for particular cases of association and then solve analytically the resulting equations. In this work, as stated in the text, a different approach was followed. The problem of solving the derivatives is addressed by using a numerical method developed by Tan et al. (2004). In their work, the numerical method that was developed lead to simply having to solve a system of linear equations. The method permitted the calculation not only of the fraction of nonbonded molecules but also its derivatives with respect to density, temperature and composition. The method, including fortran pseudo code, is very well detailed in the work of Tan et al. (2004).

B.5 Polar term: Quadrupole

A quadrupolar term can be added to account for specific interactions due to the presence of a Quadrupolar moment. The chosen quadrupolar term was the quadrupole-quadrupole one developed by Gubbins and Twu (1978), which introduces a new parameter, *Q*, the quadrupole moment. The Padé approximation of the Helmholtz energy of the perturbed quadrupole-quadrupole potencial was proposed by Stell et al (1974):

$$A^{polar} = A^{qq} = A_2^{qq} \left(\frac{1}{1 - \frac{A_3^{qq}}{A_2^{qq}}} \right) \tag{B.62}$$

The expressions for A_2 and A_3, the second and third order perturbation terms, were derived by Two (1976) and Twu et al. (1975).

$$A_2^{qq} = \frac{-1\,4\pi N \rho}{5\,k_B T} \sum_i \sum_j x_i x_j \frac{Q_i^2 Q_j^2}{\sigma_{ij}^7} J_{ij}^{(1\,0)} \tag{B.63}$$

$$A_3^{qq} = \frac{-1\,4\,4\pi N \rho}{2\,4\,5 (k_B T)^2} \sum_i \sum_j x_i x_j \frac{Q_i^3 Q_j^3}{\sigma_{ij}^{1\,2}} J_{ij}^{(1\,5)} \tag{B.64}$$

The term J runs over two and three molecule correlation functions for the reference fluid. The integrals were calculated using molecular dynamics data for a pure Lennard-Jones fluid and the resulting values were fitted to simple functions of temperature and density.

$$\left|J^{(n)}\right| = A_n \rho^2 \ln T + B_n \rho^2 + C_n \rho \ln T + D_n \rho + E_n \ln T + F_n \tag{B.65}$$

This term was only applied to the soft-SAFT version.

APPENDIX C

Additional calculations made for poly(ethylene glycol) mixtures with carbon dioxide and propane.

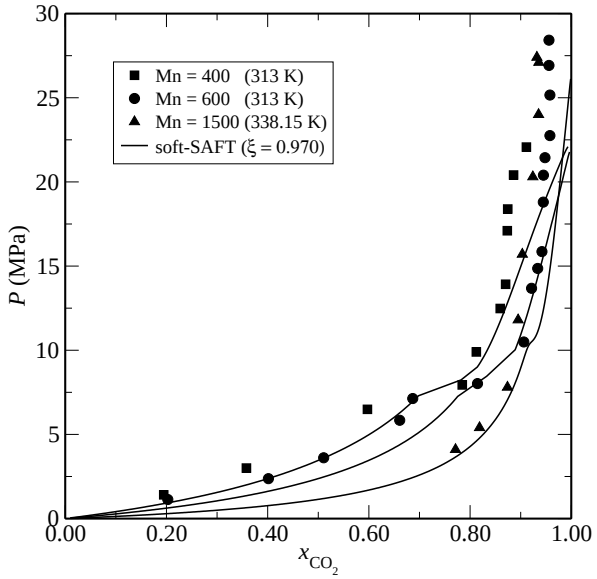

Figure C.1. Description of the soft-SAFT EoS of the vapor-liquid equilibria of the mixture poly(ethylene glycol) / carbon dioxide. Experimental data is from Daneshvar et al., (1990) (400 and 600 g/mol) and Wiesmet et al., (2001) (1500 g/mol)

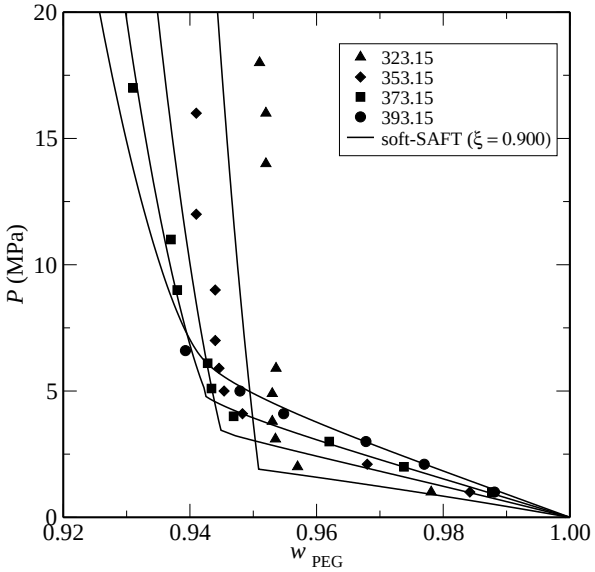

Figure C.2. Model description of the mixture PEG 1500 / propane by the soft-SAFT EoS. Experimental data from Wiesmet et al. (2001)

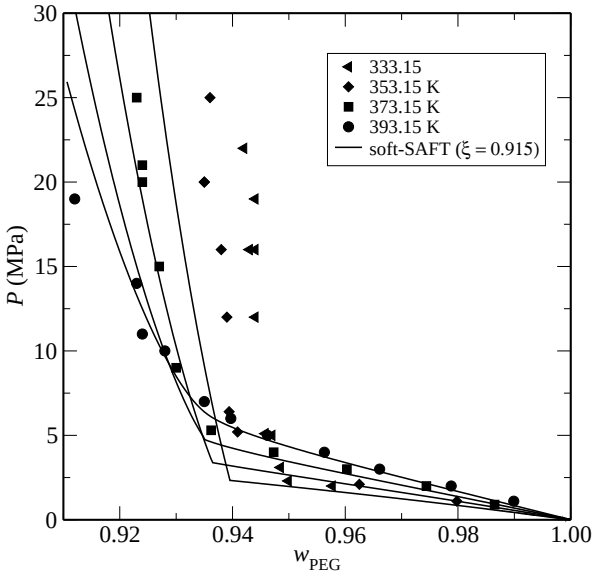

Figure C.3. Description of the vapor-liquid phase equilibria by the soft-SAFT EoS of the system PEG 4000 / propane. Experimental data from Wiesmet et al. (2001)

Publication List

Pedrosa, N.; Gao, J.; Marrucho, I. M.; Coutinho, J. A. P. *Correlation of Solvent Activities in Polymer Solutions: a Comparison of Models*; Fluid Phase Equilibria, 219, 129-138, **2004.**

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